## **Section IV**

## ORGANIC MOLECULAR FUNCTIONAL GROUPS AND MOLECULES

5 Organic molecules comprising an arbitrary number of atoms can be solved using the similar principles and procedures as those used to solve alkanes of arbitrary length. Alkanes can be considered to be comprised of the functional groups of  $CH_3$ ,  $CH_2$ , and C-C. These groups with the corresponding geometrical parameters and energies can be added as a linear sum to give the solution of any straight chain alkane as shown in the Continuous-Chain Alkanes 10 section. Similarly, the geometrical parameters and energies of all functional groups such as alkanes, branched alkanes, alkenes, branched alkenes, alkyl fluorides, alkyl chlorides, alkyl bromides, alkyl iodides, alkene halides, primary alcohols, secondary alcohols, tertiary alcohols, ethers, primary amines, secondary amines, tertiary amines, aldehydes, ketones, carboxylic acids, carboxylic esters, amides, N-alkyl amides, N,N-dialkyl amides, 15 urea, acid halides, acid anhydrides, nitriles, thiols, sulfides, disulfides, sulfoxides, sulfones, sulfites, sulfates, nitro alkanes, nitrites, nitrates, conjugated polyenes, aromatics, heterocyclic aromatics, substituted aromatics, and others can be solved. The functional-group solutions can be made into a linear superposition and sum, respectively, to give the solution of any organic molecule. The solutions of the functional groups can be conveniently obtained by 20 using generalized forms of the geometrical and energy equations. The equations and sections that are referenced by not contained in this text refer to those sections and equations of the book by R. L. Mills entitled, "The Grand Unified Theory of Classical Quantum Mechanics", June 2006 Edition, Cadmus Professional Communications-Science Press Division, Ephrata, PA, ISBN 0963517171, Library of Congress Control Number 2005936834; posted at 25 http://www.blacklightpower.com/bookdownload.shtml which is incorporated in its entirety by reference.

Consider the case wherein at least two atomic orbital hybridize as a linear combination of electrons at the same energy in order to achieve a bond at an energy minimum, and the sharing of electrons between two or more such orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. The force generalized constant k' of a

H<sub>2</sub>-type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{C_1 C_2 2e^2}{4\pi\varepsilon_0} \tag{15.1}$$

where  $C_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the molecule or molecular ion which is 0.75 (Eq. (13.59)) in the case of H bonding to a 5 central atom and 0.5 (Eq. (14.152)) otherwise, and  $C_2$  is the factor that results in an equipotential energy match of the participating at least two molecular or atomic orbitals of the chemical bond. From Eqs. (13.58-13.63), the distance from the origin of the MO to each focus c' is given by:

$$c' = a\sqrt{\frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}}$$
 (15.2)

10 The internuclear distance is

$$2c' = 2\sqrt{\frac{aa_0}{2C_1C_2}} \tag{15.3}$$

The length of the semiminor axis of the prolate spheroidal MO b = c is given by

$$b = \sqrt{a^2 - c'^2} \tag{15.4}$$

And, the eccentricity, e, is

$$e = \frac{c'}{a} \tag{15.5}$$

From Eqs. (11.207-11.212), the potential energy of the two electrons in the central field of the nuclei at the foci is

$$V_{e} = n_{1}c_{1}c_{2}\frac{-2e^{2}}{8\pi\varepsilon_{0}\sqrt{a^{2} - b^{2}}}\ln\frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}}$$
(15.6)

The potential energy of the two nuclei is

$$V_{p} = n_{1} \frac{e^{2}}{8\pi\varepsilon_{o} \sqrt{a^{2} - b^{2}}}$$
 (15.7)

The kinetic energy of the electrons is

20

$$T = n_1 c_1 c_2 \frac{\hbar^2}{2m \ a \sqrt{a^2 - b^2}} \ln \frac{a + \sqrt{a^2 - b^2}}{a - \sqrt{a^2 - b^2}}$$
(15.8)

And, the energy,  $V_m$ , of the magnetic force between the electrons is

$$V_{m} = n_{1}c_{1}c_{2} \frac{-\hbar^{2}}{4m_{e}a\sqrt{a^{2}-b^{2}}} \ln \frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}}$$
(15.9)

The total energy of the  $H_2$ -type prolate spheroidal MO,  $E_T(\mu_1 MO)$ , is given by the sum of the energy terms:

$$E_{T}(\mu_{s}MO) = V_{e} + T + V_{m} + V_{p} \tag{15.10}$$

$$E_{T}(H_{2}MO) = -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2}-b^{2}}} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{a^{2}-b^{2}}}{a - \sqrt{a^{2}-b^{2}}} - 1 \right]$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{0}c'} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right]$$
(15.11)

5

where  $n_1$  is the number of equivalent bonds of the MO and applies in the case of functional groups. In the case of independent MOs not in contact with the bonding atoms, the terms based on charge are multiplied by  $c_{BO}$ , the bond-order factor. It is 1 for a single bond, 4 for an independent double bond as in the case of the  $CO_2$  and  $NO_2$  molecules, and 9 for an 10 independent triplet bond. Then, the kinetic energy term is multiplied by  $c'_{BO}$  which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond.  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of an MO which is 0.75 (Eqs. (13.67-13.73)) in the case of H bonding to an unhybridized central atom and 1 otherwise, and  $c_2$  is the factor that results in an equipotential energy match of the participating the MO and the at least two atomic orbitals 15 of the chemical bond. Specifically, to meet the equipotential condition and energy matching conditions for the union of the  $H_2$ -type-ellipsoidal-MO and the HOs or AOs of the bonding atoms, the factor  $c_2$  of a  $H_2$ -type ellipsoidal MO may given by (i) one, (ii) the ratio of the Coulombic or valence energy of the AO or HO of at least one atom of the bond and 13.605804 eV, the Coulombic energy between the electron and proton of H, (iii) the ratio of 20 the valence energy of the AO or HO of one atom and the Coulombic energy of another, (iv) the ratio of the valence energies of the AOs or HOs of two atoms, (v) the ratio of two  $c_2$ factors corresponding to any of cases (ii)-(iv), and (vi) the product of two different  $c_2$  factors corresponding to any of the cases (i)-(v). Specific examples of the factor  $c_2$  of a  $H_2$ -type ellipsoidal MO given in previous sections are

25 0.936127, the ratio of the ionization energy of N 14.53414 eV and 13.605804 eV, the Coulombic energy between the electron and proton of H;

0.91771, the ratio of 14.82575 
$$eV$$
,  $-E_{Coulomb}(C,2sp^3)$ , and 13.605804  $eV$ ;

0.87495, the ratio of 15.55033  $eV$ ,  $-E_{Coulomb}(C_{ethane},2sp^3)$ , and 13.605804  $eV$ ;

0.85252, the ratio of 15.95955  $eV$ ,  $-E_{Coulomb}(C_{ethylene},2sp^3)$ , and 13.605804  $eV$ ;

0.85252, the ratio of 15.95955  $eV$ ,  $-E_{Coulomb}(C_{ethylene},2sp^3)$ , and 13.605804  $eV$ ; and 0.86359, the ratio of 15.55033  $eV$ ,  $-E_{Coulomb}(C_{olkane},2sp^3)$ , and 13.605804  $eV$ .

In the generalization of the hybridization of at least two atomic-orbital shells to form a shell of hybrid orbitals, the hybridized shell comprises a linear combination of the electrons of the atomic-orbital shells. The radius of the hybridized shell is calculated from the total Coulombic energy equation by considering that the central field decreases by an integer for each successive electron of the shell and that the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons. The total energy  $E_T$  (atom,  $msp^3$ ) (m is the integer of the valence shell) of the AO electrons and the hybridized shell is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least one AO shell.

15 
$$E_T(atom, msp^3) = -\sum_{m=1}^{n} IP_m$$
 (15.12)

where  $IP_m$  is the *m*th ionization energy (positive) of the atom. The radius  $r_{msp^3}$  of the hybridized shell is given by:

$$r_{msp^3} = \sum_{q=Z-n}^{Z-1} \frac{-(Z-q)e^2}{8\pi\varepsilon_0 E_T \left(atom, msp^3\right)}$$
(15.13)

Then, the Coulombic energy  $E_{Coulomb}$  (atom,  $msp^3$ ) of the outer electron of the atom  $msp^3$ 20 shell is given by

$$E_{Coulomb}\left(atom, msp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}}$$
(15.14)

In the case that during hybridization at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) at the initial radius r of the AO electron:

25 
$$E(magnetic) = \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r^3} = \frac{8\pi\mu_0 \mu_B^2}{r^3}$$
 (15.15)

Then, the energy  $E(atom, msp^3)$  of the outer electron of the  $atom msp^3$  shell is given by the sum of  $E_{Coulomb}(atom, msp^3)$  and E(magnetic):

$$E(atom, msp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}r^{3}}$$
(15.16)

Consider next that the at least two atomic orbitals hybridize as a linear combination of 5 electrons at the same energy in order to achieve a bond at an energy minimum with another atomic orbital or hybridized orbital. As a further generalization of the basis of the stability of the MO, the sharing of electrons between two or more such hybridized orbitals to form a MO permits the participating hybridized orbitals to decrease in energy through a decrease in the radius of one or more of the participating orbitals. In this case, the total energy of the 10 hybridized orbitals is given by the sum of  $E(atom, msp^3)$  and the next energies of successive ions of the atom over the n electrons comprising the total electrons of the at least two initial AO shells. Here,  $E(atom, msp^3)$  is the sum of the first ionization energy of the atom and the hybridization energy. An example of  $E(atom, msp^3)$  for  $E(C, 2sp^3)$  is given in Eq. (14.503) where the sum of the negative of the first ionization energy of C,  $-11.27671 \, eV$ , plus the 15 hybridization energy to form the  $C2sp^3$  shell given by Eq. (14.146) is  $E(C, 2sp^3) = -14.63489 \, eV$ .

Thus, the sharing of electrons between two  $atom \, msp^3$  HOs to form an atom-atom-bond MO permits each participating hybridized orbital to decrease in radius and energy. In order to further satisfy the potential, kinetic, and orbital energy relationships, each  $atom \, msp^3$  20 HO donates an excess of 25% per bond of its electron density to the atom-atom-bond MO to form an energy minimum wherein the atom-atom bond comprises one of a single, double, or triple bond. In each case, the radius of the hybridized shell is calculated from the Coulombic energy equation by considering that the central field decreases by an integer for each successive electron of the shell and the total energy of the shell is equal to the total Coulombic energy of the initial AO electrons plus the hybridization energy. The total energy  $E_T$  (mol atom,  $msp^3$ ) (m is the integer of the valence shell) of the HO electrons is given by the sum of energies of successive ions of the atom over the n electrons comprising total electrons of the at least one initial AO shell and the hybridization energy:

$$E_{T}\left(mol.atom, msp^{3}\right) = E\left(atom, msp^{3}\right) - \sum_{m=2}^{n} IP_{m}$$
(15.17)

where  $IP_m$  is the *m*th ionization energy (positive) of the atom and the sum of  $-IP_1$  plus the hybridization energy is  $E\left(atom, msp^3\right)$ . Thus, the radius  $r_{msp}$ , of the hybridized shell is given by:

5 
$$r_{msp^3} = \left(\sum_{q=Z-n}^{Z-1} (Z-q) - s(0.25)\right) \frac{-e^2}{8\pi\varepsilon_0 E_T \left(mol.atom, msp^3\right)}$$
 (15.18)

where s = 1, 2, 3 for a single, double, and triple bond, respectively. The Coulombic energy  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>) of the outer electron of the atom msp<sup>3</sup> shell is given by

$$E_{Coulomb}\left(mol.atom, msp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp}},$$
(15.19)

In the case that during hybridization at least one of the spin-paired AO electrons is unpaired 10 in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) at the initial radius r of the AO electron given by Eq. (15.15). Then, the energy  $E(mol.atom, msp^3)$  of the outer electron of the  $atom\ msp^3$  shell is given by the sum of  $E_{Coulomb}(mol.atom, msp^3)$  and E(magnetic):

$$E\left(mol.atom, msp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{msp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}r^{3}}$$
(15.20)

15  $E_r$  (atom – atom,  $msp^3$ ), the energy change of each atom  $msp^3$  shell with the formation of the atom-atom-bond MO is given by the difference between  $E(mol.atom, msp^3)$  and  $E(atom, msp^3)$ :

$$E_{T}(atom - atom, msp^{3}) = E(mol.atom, msp^{3}) - E(atom, msp^{3})$$
(15.21)

As examples from prior sections,  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>) is one of:

20 
$$E_{Coulomb}\left(C_{ethylene}, 2sp^3\right)$$
,  $E_{Coulomb}\left(C_{ethons}, 2sp^3\right)$ ,  $E_{Coulomb}\left(C_{acetylene}, 2sp^3\right)$ , and  $E_{Coulomb}\left(C_{alkane}, 2sp^3\right)$ ;

$$E_{Coulomb}$$
 (atom, msp<sup>3</sup>) is one of  $E_{Coulomb}$  (C, 2sp<sup>3</sup>) and  $E_{Coulomb}$  (Cl, 3sp<sup>3</sup>);

$$E(mol.atom, msp^3)$$
 is one of  $E(C_{ethylene}, 2sp^3)$ ,  $E(C_{ethane}, 2sp^3)$ ,  $E(C_{ethane}, 2sp^3)$ ;

$$E(atom, msp^3)$$
 is one of and  $E(C, 2sp^3)$  and  $E(Cl, 3sp^3)$ ;

$$E_r$$
 (atom – atom,  $msp^3$ ) is one of  $E(C-C,2sp^3)$ ,  $E(C=C,2sp^3)$ , and  $E(C\equiv C,2sp^3)$ ;

5  $atom msp^3$  is one of  $C2sp^3$ ,  $Cl3sp^3$ 

$$E_T$$
  $\left(atom-atom(s_1), msp^3\right)$  is  $E_T\left(C-C, 2sp^3\right)$  and  $E_T\left(atom-atom(s_2), msp^3\right)$  is  $E_T\left(C=C, 2sp^3\right)$ , and

$$r_{msp}$$
 is one of  $r_{C2sp^3}$ ,  $r_{ethane2sp^3}$ ,  $r_{ethylene2sp^3}$ ,  $r_{acetylene2sp^3}$ ,  $r_{alkane2sp^3}$ , and  $r_{Cl3sp^3}$ .

In the case of the C2sp3 HO, the initial parameters (Eqs. (14.142-14.146)) are

10 
$$r_{2sp}^{3} = \sum_{n=2}^{5} \frac{(Z-n)e^{2}}{8\pi\varepsilon_{0} \left(e148.25751 \ eV\right)} = \frac{10e^{2}}{8\pi\varepsilon_{0} \left(e148.25751 \ eV\right)} = 0.91771a_{0}$$
 (15.22)

$$E_{Coulomb}\left(C, 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{2sp^{3}}} = \frac{-e^{2}}{8\pi\varepsilon_{0}0.91771a_{0}} = -14.82575 \ eV \tag{15.23}$$

$$E(magnetic) = \frac{2\pi\mu_0 e^2 h^2}{m_e^2 (r_3)^3} = \frac{8\pi\mu_0 \mu_B^2}{(0.84317a_0)^3} = 0.19086 \text{ eV}$$
 (15.24)

$$E(C,2sp^{3}) = \frac{-e^{2}}{8\pi\epsilon_{0}r_{2\varphi^{3}}} + \frac{2\pi\mu_{0}e^{2}h^{2}}{m_{e}^{2}(r_{3})^{3}}$$

$$= -14.82575 \ eV + 0.19086 \ eV$$

$$= -14.63489 \ eV$$
(15.25)

In Eq. (15.18),

15 
$$\sum_{q=Z-n}^{Z-1} (Z-q) = 10$$
 (15.26)

Eqs. (14.147) and (15.17) give

$$E_T$$
 (mol.atom, msp<sup>3</sup>) =  $E_T$  ( $C_{ethane}$ , 2sp<sup>3</sup>) = -151.61569 eV (15.27)

Using Eqs. (15.18-15.28), the final values of  $r_{C2sp^3}$ ,  $E_{Coulomb}(C2sp^3)$ , and  $E(C2sp^3)$ , and the resulting  $E_r(C^{BO}_{-C},C2sp^3)$  of the MO due to charge donation from the HO to the MO where

C-C refers to the bond order of the carbon-carbon bond for different values of the parameter s are given in Table 15.1.

Table 15.1. The final values of  $r_{C2sp^3}$ ,  $E_{Coulomb}(C2sp^3)$ , and  $E(C2sp^3)$  and the resulting  $E_r(C^{BO}_r, C^{CO}_r)$  of the MO due to charge donation from the HO to the MO where  $C^{BO}_r$  refers to the bond order of the carbon-carbon bond.

MO Bond Order	s 1	s 2	$r_{C2sp^3}\left(a_0\right)$	$E_{Coulomb}\left(C2sp^3\right)$	$E(C2sp^3)$	$E_T \left( C - C, C2sp^3 \right)$
(BO)			Final	(eV) Final	(eV) Final	(eV)
I	1	0	0.87495	-15.55033	-15.35946	-0.72457
II	2	0	0.85252	-15.95955	-15.76868	-1.13379
Ш	3	0	0.83008	-16.39089	-16.20002	-1.56513
IV	4	0	0.80765	-16.84619	-16.65532	-2.02043

In another generalized case of the basis of forming a minimum-energy bond with the constraint that it must meet the energy matching condition for all MOs at all HOs or AOs, the energy  $E(mol.atom, msp^3)$  of the outer electron of the atom  $msp^3$  shell of each bonding atom must be the average of  $E(mol.atom, msp^3)$  for two different values of s:

$$E(mol.atom, msp^3) = \frac{E(mol.atom(s_1), msp^3) + E(mol.atom(s_2), msp^3)}{2}$$
(15.28)

In this case,  $E_T(atom-atom,msp^3)$ , the energy change of each  $atom\ msp^3$  shell with the formation of each atom-atom-bond MO, is average for two different values of s:

15 
$$E_T \left( atom - atom, msp^3 \right) = \frac{E_T \left( atom - atom \left( s_1 \right), msp^3 \right) + E_T \left( atom - atom \left( s_2 \right), msp^3 \right)}{2}$$
 (15.29)

Consider an aromatic molecule such as benzene given in the Benzene Molecule section. Each C = C double bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two  $C2sp^3$  HOs of the participating carbon atoms. Each C - H bond of CH having two spin-paired electrons, one from an initially unpaired electron of the carbon atom and the other from the hydrogen atom, comprises the

linear combination of 75%  $H_2$ -type ellipsoidal MO and 25%  $C2sp^3$  HO as given by Eq. (13.439). However,  $E_T(atom-atom,msp^3)$  of the C-H-bond MO is given by  $0.5E_T(C=C,2sp^3)$  (Eq. (14.247)) corresponding to one half of a double bond that matches the condition for a single-bond order for C-H that is lowered in energy due to the aromatic character of the bond.

A further general possibility is that a minimum-energy bond is achieved with satisfaction of the potential, kinetic, and orbital energy relationships by the formation of an MO comprising an allowed multiple of a linear combination of  $H_2$ -type ellipsoidal MOs and corresponding HOs or AOs that contribute a corresponding allowed multiple (e.g. 0.5, 0.75, 10 1) of the bond order given in Table 15.1. For example, the alkane MO given in the Continuous-Chain Alkanes section comprises a linear combination of factors of 0.5 of a single bond and 0.5 of a double bond.

Consider a first MO and its HOs comprising a linear combination of bond orders and a second MO that shares a HO with the first. In addition to the mutual HO, the second MO 15 comprises another AO or HO having a single bond order or a mixed bond order. Then, in order for the two MOs to be energy matched, the bond order of the second MO and its HOs or its HO and AO is a linear combination of the terms corresponding to the bond order of the mutual HO and the bond order of the independent HO or AO. Then, in general,  $E_T$  (atom – atom,  $msp^3$ ), the energy change of each atom  $msp^3$  shell with the formation of 20 each atom-atom-bond MO, is a weighted linear sum for different values of s that matches the energy of the bonded MOs, HOs, and AOs:

$$E_{T}\left(atom - atom, msp^{3}\right) = \sum_{n=1}^{N} c_{s_{n}} E_{T}\left(atom - atom\left(s_{n}\right), msp^{3}\right)$$
 (15.30)

where  $c_{s_n}$  is the multiple of the BO of  $s_n$ . The radius  $r_{msp^3}$  of the atom  $msp^3$  shell of each bonding atom is given by the Coulombic energy using the initial energy  $E_{Coulomb}$  (atom,  $msp^3$ ) and  $E_T$  (atom – atom,  $msp^3$ ), the energy change of each atom  $msp^3$  shell with the formation of each atom-atom-bond MO:

$$r_{msp^3} = \frac{-e^2}{8\pi\varepsilon_0 a_0 \left( E_{Coulonb} \left( atom, msp^3 \right) + E_T \left( atom - atom, msp^3 \right) \right)}$$
(15.31)

where  $E_{Coulomb}(C2sp^3) = -14.825751 \ eV$ . The Coulombic energy  $E_{Coulomb}(mol.atom, msp^3)$  of the outer electron of the  $atom \ msp^3$  shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy  $E(mol.atom, msp^3)$  of the outer electron of the  $atom \ msp^3$  shell is given by the sum of  $E_{Coulomb}(mol.atom, msp^3)$  and E(magnetic) (Eq. (15.20)).  $E_T(atom - atom, msp^3)$ , the energy change of each  $atom \ msp^3$  shell with the formation of the atom-atom-bond MO is given by the difference between  $E(mol.atom, msp^3)$  and  $E(atom, msp^3)$  given by Eq. (15.21). Using Eq. (15.23) for  $E_{Coulomb}(C, 2sp^3)$  in Eq. (15.31), the single bond order energies given by Eqs. (15.18-15.27) and shown in Table 15.1, and the linear combination energies (Eqs. (15.28-15.30)), the parameters of linear combinations of bond orders and linear combinations of mixed bond orders are given in Table 15.2.

15 Table 15.2. The final values of  $r_{C2sp^3}$ ,  $E_{Coulomb}(C2sp^3)$ , and  $E(C2sp^3)$  and the resulting  $E_T\left(C^{BO}_{-C},C2sp^3\right)$  of the MO comprising a linear combination of  $H_2$ -type ellipsoidal MOs and corresponding HOs of single or mixed bond order where  $c_{s_n}$  is the multiple of the bond order parameter  $E_T\left(atom-atom(s_n),msp^3\right)$  given in Table 15.1.

Table	15.	1					455			,
МО	s									
Bond	1	$c_{s_1}$	<i>s</i> 2	$C_{s_2}$	<i>s</i> 3	$c_{s_3}$	$r_{C2sp^3}\left(a_0\right)$	$E_{Coulomb}\left(C2sp^3\right)$	$E(C2sp^3)$	$E_{-}$ $\begin{pmatrix} BO \\ C - C \cdot C \cdot S \cdot p^3 \end{pmatrix}$
Order	٠		2		3		•-	(eV)	(eV)	
(BO)							Final	Final	Final	(eV)
(DO)										
1/21	1	0.5	0	0	0	0	0.89582	-15.18804	-14.99717	-0.36228
1/211	2	0.5	0	0	0	0	0.88392	-15.39265	-15.20178	-0.56689
<b>I</b> +	1	0.5	2	0.2	0	0	0.87941	-15.47149	-15.28062	-0.64573
1/211				5						
1/2II	2	0.2	1	0.2	2	0.2	0.87363	-15.57379	-15.38293	-0.74804
+ (I +		5		5		5				
II)										
3/4II	2	0.7	0	0	0	0	0.86793	-15.67610	-15.48523	-0.85034
		5						·		
I + II	1	0.5	2	0.5	0	0	0.86359	-15.75493	-15.56407	-0.92918
I +	, 1	0.5	3	0.5	0	0	0.85193	-15.97060	-15.77974	-1.14485
Ш										
I +	1	0.5	4	0.5	0	0	0.83995	-16.19826	-16.00739	-1.37250
IV										
II +	2	0.5	3	0.5	0	.0	0.84115	-16.17521	-15.98435	-1.34946
Ш										
II +	2	0.5	4	0.5	0	0	0.82948	-16.40286	-16.21200	-1.57711
IV										
111 +	3	0.5	4	0.5	0	0	0.81871	-16.61853	-16.42767	-1.79278
IV ·										
IV+	4	0.5	4	0.5	0	0	0.80765	-16.84619	-16.65532	-2.02043
IV									•	

Consider next the radius of the AO or HO due to the contribution of charge to more than one bond. The energy contribution due to the charge donation at each atom such as 5 carbon superimposes linearly. In general, the radius  $r_{mol2sp^3}$  of the  $C2sp^3$  HO of a carbon atom of a given molecule is calculated using Eq. (14.514) by considering  $\sum E_{T_{mol}} (MO, 2sp^3)$ , the total energy donation to each bond with which it participates in bonding. The general equation for the radius is given by

$$r_{mol2sp^{3}} = \frac{-e^{2}}{8\pi\varepsilon_{0} \left(E_{Coulomb}\left(C, 2sp^{3}\right) + \sum E_{T_{mol}}\left(MO, 2sp^{3}\right)\right)}$$

$$= \frac{e^{2}}{8\pi\varepsilon_{0} \left(e14.825751 \ eV + \sum \left|E_{T_{mol}}\left(MO, 2sp^{3}\right)\right|\right)}$$
(15.32)

The Coulombic energy  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>) of the outer electron of the atom msp<sup>3</sup> shell is given by Eq. (15.19). In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy  $E(mol.atom, msp^3)$  of the outer electron of the atom  $msp^3$  shell is given by the sum of  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>) and E(magnetic) (Eq. (15.20)).

For example, the  $C2sp^3$  HO of each methyl group of an alkane contributes  $10 -0.92918 \, eV$  (Eq. (14.513)) to the corresponding single C-C bond; thus, the corresponding  $C2sp^3$  HO radius is given by Eq. (14.514). The  $C2sp^3$  HO of each methylene group of  $C_nH_{2n+2}$  contributes  $-0.92918 \, eV$  to each of the two corresponding C-C bond MOs. Thus, the radius (Eq. (15.32)), the Coulombic energy (Eq. (15.19)), and the energy (Eq. (15.20)) of each alkane methylene group are

$$r_{alkaneC_{methylene} 2sp^{3}} = \frac{-e^{2}}{8\pi\varepsilon_{0} \left(E_{Coulomb} \left(C, 2sp^{3}\right) + \sum E_{T_{alkane}} \left(methylene \ C - C, 2sp^{3}\right)\right)}$$

$$= \frac{e^{2}}{8\pi\varepsilon_{0} \left(e14.825751 \ eV + e0.92918 \ eV + e0.92918 \ eV\right)}$$

$$= 0.81549a_{0}$$
(15.33)

$$E_{Coulomb} \left( C_{methylene} 2 s p^3 \right) = \frac{-e^2}{8 \pi \varepsilon_0 \left( 0.81549 a_0 \right)} = -16.68412 \ eV \tag{15.34}$$

$$E\left(C_{methylene} 2sp^{3}\right) = \frac{-e^{2}}{8\pi\varepsilon_{0}\left(0.81549a_{0}\right)} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}\left(0.84317a_{0}\right)^{3}} = -16.49325 \ eV \tag{15.35}$$

In the determination of the parameters of functional groups, heteroatoms bonding to  $C2sp^3$  HOs to form MOs are energy matched to the  $C2sp^3$  HOs. Thus, the radius and the 20 energy parameters of a bonding heteroatom are given by the same equations as those for

 $C2sp^3$  HOs. Using Eqs. (15.15), (15.19-15.20), (15.24), and (15.32) in a generalized fashion, the final values of the radius of the HO or AO,  $r_{Atom.HO.AO}$ ,  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>), and  $E(C_{mol}2sp^3)$  are calculated using  $\sum E_{T_{group}}$  (MO,2sp<sup>3</sup>), the total energy donation to each bond with which an atom participates in bonding corresponding to the values of  $E_r(C^{BO}_{-C,C2sp^3})$  of the MO due to charge donation from the AO or HO to the MO given in Tables 15.1 and 15.2.

Table 15.3.A. The final values of  $r_{Atom.HO.AO}$ ,  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>), and  $E(C_{mol}2sp^3)$  calculated using the values of  $E_T(C_{-C,C2sp^3}^{BO})$  given in Tables 15.1 and 15.2.

													-4:	58							_								
26	25	24	23	22	21	20	19	18	17	16	15	14	13	13	Ξ	10	9	8	7	6	5	4	w	2	1	ion	Designat	ation	Hybridiz
-2.02043	-0.92918	-1.13379	-1.79278	-0.85035	-0.72457	-1.57711	-0.64574	-1.56513	-0.82688	-0.5669	-0.72457	-0.46459	-1.3725	-1.34946	-0.46459	-1.14485	-1.13379	-0.54343	-0.92918	-0.85034	-0.72457	-0.56689	-0.46459	-0.36229	0				$E_T\left(C-C,C2sp^3\right)$
0	-0.92918	-0.72457	0	-0.85035	-0.92918	0	-0.92918	Ō	-0.72457	-0.92918	-0.72457	-0.92918	0	0	-0.82688	0	0	-0.54343	0	0	0	0	0	0	0				$E_T\left(C-C,C2sp^3\right)$
0	0	0	0	0	0	0	0	0	0	С	0	0	0	0	0	0	0	О	0	0	0	0	0	0	0				$E_T\left(C-C,C2sp^3\right)$
0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0				$E_T\bigg(C-C,C2sp^3\bigg)\bigg  E_T\bigg(C-C,C2sp^3\bigg)\bigg  E_T\bigg(C-C,C2sp^3\bigg)\bigg  E_T\bigg(C-C,C2sp^3\bigg)\bigg  E_T\bigg(C-C,C2sp^3\bigg)\bigg  E_T\bigg(C-C,C2sp^3\bigg)\bigg  E_T\bigg(C-C,C2sp^3\bigg)\bigg $
0	0	Û	0	0	0	. 0	0 .	0	0	0	0 .	0	0	0	0	0	0	0	0	0	0	0	0	0	0				$E_r \left( C - C, C2sp^3 \right)$
0.80765	0.81549	0.81549	0.81871	0.82327	0.82562	0.82948	0.82959	0.83008	0.83078	0.8336	0.836	0.83885	0.83995	0.84115	0.84418	0.85193	0.85252	0.85503	0.86359	0.86793	0.87495	0.88392	0.88983	0.89582	0.91771			Final	Atom.HO.AO
-16.84619	-16.68412	-16.68411	-16.61853	-16.52645	16.47951	-16.40286	-16.40067	-16.39089	-16.37721	-16.32183	-16.2749	-16.21952	-16.19826	-16.17521	-16.11722	-15.9706	-15.95955	-15.91261	-15.75493	-15.6761	-15.55033	-15.39265	-15.29034	-15.18804	-14.82575	,	Final	e\$	$E_{Coulomb}$ (miol.atom, insp <sup>3</sup> ) $E(C_{red}2sp^3)$
-16.65532	-16.49325	-16.49325	-16.42767	-16.33559	-16.28865	-16.212	-16.20981	-16.20002	-16.18634	-16.13097	-16.08404	-16.02866	-16.00739	-15.98435	-15.92636	-15.77974	-15.76868	-15.72175	-15.56407	-15.48523	-15.35946	-15.20178	-15.09948	-14.99717	-14.63489		Final	(e <	$E(C_{max}2sp^3)$

_	_		_		_		45	9																			
2	ŝ	40	48	47	46	: :	45	\$ 2	3 2	3 :	4	40	39	38	37		33	35	34	33	32	ы	۲	30	29	28	//
-1./32/0	1 70778	_1 12270	-0.82688	-0.46459	-1.1338	-0.60034	0.05024	1 74046	0.1676.0-	0.020.0	88968 0-	-0 92918	-0.54343	-0.92918	-0.72457	0.02000	88908 0	-0.72457	-0.85035	-0.64574	-0.46459	-1.34946	-1.133/9	1 12270	0595 U-	-0.85035	-1.13379
-0.92918	-1.133/9	1 12270	34046	-0.85035	-0.92918	-0.54343	-0.043/4	-0.54343	-0.92918	-0.92918	0.00001	-0.85024	-0.54343	-0.72457	-0.92918	-U.12431	072457	D 77/457	D 5660	-0.880-	-0.92918	-0.92918	-1.13379	-0.12437	CSACE	-0.88035	-0.92918
-0.92918	-1.13379	0.525.0-	0.00010	-0.85035	-0.92918	-0.60631	-0.92918	-0.5669	-0.92918	-0.92918	70.03034	0 0 0 0 0 0	-0.5669	-0.92918	-0.92918	-0.92918	*0.92918	0.02918	-0.02010	-0.88034	-0.92918	0	0	-0.92918	-0.707.0	0 46460	0
0	0	0		-0.92918	0	-0.92918	0	-0.92918	0	0	C	0.727.10	91000	0	0	0	U	0				0	0	0	0		0
0	0	0		0	0	0	0	0	0	0	0			0	0	0	0	0	0	0		0	0	0	0		
0.73637	0.74646	0.75877	0.73924	0 76034	0.7636	0.76631	0.76652	0.76801	0.77247	0.77699	0.77945	0./8155	0.701.55	0.78144	0.78155	0.78617	0.79085	0.79232	0.79232	0.79340	0.73,740	0.70576	0.79597	0.78916	0.80076	1,900,01	123000
-18.47690	-18.22712	-17.93128	-17.92022	12 0000	-17.81791	-17.75502	-17.75013	-17.71561	-17.6133	-17.51099	-17.45561	-17.40869	K09/1-1-	17 /08/0	-17 4086R	-17.30638	-17.20408	-17.17218	-17.17217	-17.14871	-17.1044	13 104	-17.09334	-17.04641	-16.99104	-16.88872	
-18.28604	-18.03626	-17.74041	-17.72936	11.02.705	-17 62705	-17.56415	-17.55927	-17.52475	-17.42244	-17.32013	-17.26475	-17.21783	-17.21783	100100	1771787	-17.11552	-17.01322	-16.98132	-16.98131	-16,95784	-16,91353	10,70270	-16 90248	-16.85554	-16.80018	-16.69786	

Table 15.3.B. The final values of  $r_{Atom.HO.AO}$ ,  $E_{Coulomb}$  (mol.atom, msp<sup>3</sup>), and  $E(C_{mol}2sp^3)$  calculated for heterocyclic groups using the values of  $E_T(C^{BO}_TC,C2sp^3)$  given in Tables 15.1 and 15.2.

															_						_						
26	25	24	23	22	21	20	19	18	17	16	15	14	13	12	11	10	9	8	7	6	5	4	3	2	1	Designation	Atom Hybridization
-1.13379	-0.85034	-0.85034	-0.92918	-0.85034	-0.54343	-0.85035	-0.85035	-1.13379	-0.85034	-0.85035	-1.13379	-1.13379	-0.92918	-0.85035	-0.92918	-0.92918	-0.72457	-0.46459	-0.60631	-1.13379	-0.54343	-0.92918	-0.72457	-0.56690	0		$E_r\bigg(C-C,C2sp^3\bigg)$
-0.92918	-0.54343	-0.54343	-0.92918	-0.28345	-0.54343	.06995.0-	-0.54343	-1.13380	-0.85034	-0.85035	-0.92918	-0.72457	-0.92918	-0.85035	-0.72457	-0.60631	-0.72457	-0.92918	-0.60631	0	-0.54343	0	0	0	0		$E_{r}\left(C-C,C2sp^{3}\right)$ $E_{r}\left(C-C,C2sp\right)$
-0.92918	-0.60631	-0.56690	-0.92918	-0.54343	-0.56690	-0.92918	0.00000	0	-0.56690	-0.46459	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		$E_r\bigg(C-C,C2xp\bigg)$
0	-0.92918	-0.92918	0	-0.92918	-0.92918	0	-0.92918	0	0 .	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		$E_T\bigg(C-C,C2sp^3\bigg)$
0 .	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0		$E_T \left( C - C, C2sp^3 \right)$
0.76360	0.76631	0.76801	0.77247	0.78050	0.78155	0.79232	0.79340	0.79597	0.79597	0.80076	0.80561	0.81549	0.81549	0.82327	0.82562	0.83159	0.83600	0.83885	0.84833	0.85252	0.85503	0.86359	0.87495	0.88392	0.91771	Final	r <sub>Atom.HO.AO</sub>
-17.81791	-17.75502	-17.71560	-17.61330	-17.43216	-17.40869	-17.17218	-17.14871	-17.09334	-17.09334	-16.99103	-16.88873	-16.68412	-16.68411	-16.52644	-16.47951	-16.36125	-16.27490	-16.21953	-16.03838	-15.95954	-15.91261	-15.75493	-15.55033	-15.39265	-14.82575	(cV) Final	Ecouloub (mol atom, msp³)
-17.62704	-17.56416	-17.52474	-17.42243	-17.24130	-17.21783	-16.98132	-16.95785	-16.90248	-16.90247	-16.80017	-16.69786	-16.49325	-16.49325	-16.33558	-16.28864	-16.17038	-16.08404	-16.02866	-15.84752	-15.76868	-15.72175	-15.56407	-15,35946	-15.20178	-14.63489	(eV) Final	$E\left(C_{mol}2sp^3\right)$

Г		T	_	Т	_	Т		_
	30		23	3	04	30	ţ	`
	-1.13379		-1.13380		-0.46439	03/2/6	41.661.12	17770
21.001.7	-1 13379		-1.13379		-0.85035		-1.13380	1 13300
-1.10079	-1 13370	0.72.7.0	21000		-0.85035		-0.72457	
•	^	c	0		-0 92918	,	5	
C		c	,	<			0	
0.74646		0.75493		0./3924	23503	0.700	02020	
-18.22713		-18.02252		-17.92022		-17.81791		
-18.03627	77.00100	27128 712		-17.72935		-17.62705		

The energy of the MO is matched to each of the participating outermost atomic or hybridized orbitals of the bonding atoms wherein the energy match includes the energy contribution due to the AO or HO's donation of charge to the MO. The force constant k' 5 (Eq. (15.1)) is used to determine the ellipsoidal parameter c' (Eq. (15.2)) of the each  $H_2$ -type-ellipsoidal-MO in terms of the central force of the foci. Then, c' is substituted into the energy equation (from Eq. (15.11))) which is set equal to  $n_1$  times the total energy of  $H_2$  where  $n_1$  is the number of equivalent bonds of the MO and the energy of  $H_2$ ,  $-31.63536831 \, eV$ , Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO. From the energy equation and the relationship between the axes, the dimensions of the MO are solved. The energy equation has the semimajor axis a as it only parameter. The solution of the semimajor axis a then allows for the solution of the other axes of each prolate spheroid and eccentricity of each MO (Eqs. (15.3-15.5)). The parameter solutions then allow for the component and total energies of the MO to be determined.

The total energy,  $E_T(H,MO)$ , is given by the sum of the energy terms (Eqs. (15.6-15.11)) plus  $E_T(AO/HO)$ :

$$E_T(H_2MO) = V_e + T + V_m + V_p + E_T(AO/HO)$$
 (15.36)

$$E_{T}(H_{2}MO) = -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2}-b^{2}}} \left[c_{1}c_{2}\left(2-\frac{a_{0}}{a}\right)\ln\frac{a+\sqrt{a^{2}-b^{2}}}{a-\sqrt{a^{2}-b^{2}}}-1\right] + E_{T}(AO/HO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}c'} \left[c_{1}c_{2}\left(2-\frac{a_{0}}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] + E_{T}(AO/HO)$$
(15.37)

where  $n_1$  is the number of equivalent bonds of the MO,  $c_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the group,  $c_2$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of each chemical bond, and  $E_T(AO/HO)$  is the total energy comprising the difference of the energy E(AO/HO) of at least one atomic or hybrid orbital to which the MO is energy matched and any energy component  $\Delta E_{H_2MO}(AO/HO)$  due to the AO or HO's charge donation to the MO.

$$E_{T}(AO/HO) = E(AO/HO) - \Delta E_{H,MO}(AO/HO)$$
(15.38)

As specific examples given in previous sections,  $E_T(AO/HO)$  is one from the group of

$$E_T(AO/HO) = E(O2p \text{ shell}) = -E(\text{ionization}; O) = -13.6181 \text{ eV};$$

$$E_T(AO/HO) = E(N2p \text{ shell}) = -E(\text{ionization}; N) = -14.53414 \text{ eV};$$

$$E_T(AO/HO) = E(O2p \text{ shell}) = -E(\text{ionization}; N) = -14.53414 \text{ eV};$$

$$E_T(AO/HO) = E(C, 2sp^3) = -14.63489 eV;$$

5 
$$E_T(AO/HO) = E_{Coulomb}(Cl, 3sp^3) = -14.60295 \ eV;$$

$$E_{\tau}(AO/HO) = E(ionization; C) + E(ionization; C^{+});$$

$$E_T(AO/HO) = E(C_{ethane}, 2sp^3) = -15.35946 \ eV;$$

$$E_T(AO/HO) = +E(C_{ethylene}, 2sp^3) - E(C_{ethylene}, 2sp^3);$$

$$E_T(AO/HO) = E(C,2sp^3) - 2E_T(C=C,2sp^3) = -14.63489 eV - (-2.26758 eV);$$

10 
$$E_T(AO/HO) = E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) - E(C_{acetylene}, 2sp^3) = 16.20002 \ eV;$$

$$E_T(AO/HO) = E(C,2sp^3) - 2E_T(C \equiv C,2sp^3) = -14.63489 \ eV - (-3.13026 \ eV);$$

$$E_T(AO/HO) = E(C_{benzene}, 2sp^3) - E(C_{benzene}, 2sp^3);$$

$$E_T(AO/HO) = E(C, 2sp^3) - E_T(C = C, 2sp^3) = -14.63489 \text{ eV} - (-1.13379 \text{ eV}), \text{ and}$$

$$E_T(AO/HO) = E(C_{alkane}, 2sp^3) = -15.56407 eV$$
.

To solve the bond parameters and energies, 
$$c' = a \sqrt{\frac{\hbar^2 4\pi \varepsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}}$$
 (Eq.

(15.2)) is substituted into  $E_T(\mu_1MO)$  to give

$$E_{T}(H_{2}MO) = -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{a^{2} - b^{2}}} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{a^{2} - b^{2}}}{a - \sqrt{a^{2} - b^{2}}} - 1 \right] + E_{T}(AO/HO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}c'} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + c'}{a - c'} - 1 \right] + E_{T}(AO/HO)$$

$$= -\frac{n_{1}e^{2}}{8\pi\varepsilon_{o}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[ c_{1}c_{2} \left( 2 - \frac{a_{0}}{a} \right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}} - 1}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}} - 1} \right] + E_{T}(AO/HO)$$

$$(15.39)$$

The total energy is set equal to  $E(basis\ energies)$  which in the most general case is given by

the sum of a first integer  $n_1$  times the total energy of  $H_2$  minus a second integer  $n_2$  times the total energy of H, minus a third integer  $n_3$  times the valence energy of E(AO) (e.g.  $E(N) = -14.53414 \ eV$ ) where the first integer can be 1,2,3..., and each of the second and third integers can be 0,1,2,3....

E(basis energies) =  $n_1$  (-31.63536831 eV) -  $n_2$  (-13.605804 eV) -  $n_3$  E(AO) (15.40) In the case that the MO bonds two atoms other than hydrogen, E(basis energies) is  $n_1$  times the total energy of  $H_2$  where  $n_1$  is the number of equivalent bonds of the MO and the energy of  $H_2$ , -31.63536831 eV, Eq. (11.212) is the minimum energy possible for a prolate spheroidal MO:

10 
$$E(basis\ energies) = \eta_1(-31.63536831\ eV)$$
 (15.41)

 $E_T(H_1,MO)$ , is set equal to  $E(basis\ energies)$ , and the semimajor axis a is solved. Thus, the semimajor axis a is solved from the equation of the form:

$$-\frac{n_{1}e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}\left[c_{1}c_{2}\left(2-\frac{a_{0}}{a}\right)\ln\frac{a+\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a-\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}-1\right]+E_{T}\left(AO/HO\right)=E(basis\ energies)\ (15.42)$$

The distance from the origin of the  $H_2$ -type-ellipsoidal-MO to each focus c', the internuclear 15 distance 2c', and the length of the semiminor axis of the prolate spheroidal  $H_2$ -type MO b=c are solved from the semimajor axis a using Eqs. (15.2-15.4). Then, the component energies are given by Eqs. (15.6-15.9) and (15.39).

The total energy of the MO of the functional group,  $E_T$  (MO), is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms and  $E_T$  (atom—atom, msp³.AO), the change in the energy of the AOs or HOs upon forming the bond. From Eqs. (15.39-15.40),  $E_T$  (MO) is

$$E_T(MO) = E(basis\ energies) + E_T(atom-atom, msp^3.AO)$$
 (15.43)

During bond formation, the electrons undergo a reentrant oscillatory orbit with vibration of the nuclei, and the corresponding energy  $\overline{E}_{osc}$  is the sum of the Doppler,  $\overline{E}_{D}$ , and 25 average vibrational kinetic energies,  $\overline{E}_{Kvib}$ :

$$\overline{E}_{osc} = n_{l} \left( \overline{E}_{D} + \overline{E}_{Kvib} \right) = n_{l} \left( E_{hv} \sqrt{\frac{2\overline{E}_{K}}{m_{e}c^{2}}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$

$$(15.44)$$

where  $n_1$  is the number of equivalent bonds of the MO, k is the spring constant of the equivalent harmonic oscillator, and  $\mu$  is the reduced mass. The angular frequency of the reentrant oscillation in the transition state corresponding to  $\overline{E}_D$  is determined by the force 5 between the central field and the electrons in the transition state. The force and its derivative are given by

$$f\left(R\right) = -c_{BO} \frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3} \tag{15.45}$$

and

$$f'(a) = 2c_{BO} \frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}$$
 (15.46)

10 such that the angular frequency of the oscillation in the transition state is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{m_e}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_{1o}C_{2o}e^2}{4\pi\epsilon_0 R^3}}{m_e}}$$
(15.47)

where R is the semimajor axis a or the semiminor axis b depending on the eccentricity of the bond that is most representative of the oscillation in the transition state,  $c_{BO}$  is the bond-order factor which is 1 for a single bond and when the MO comprises  $n_1$  equivalent single bonds as in the case of functional groups.  $c_{BO}$  is 4 for an independent double bond as in the case of the  $CO_2$  and  $NO_2$  molecules and 9 for an independent triplet bond.  $C_{1o}$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of the oscillatory transition state of a chemical bond of the group, and  $C_{2o}$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond. 20 Typically,  $C_{1o} = C_1$  and  $C_{2o} = C_2$ . The kinetic energy,  $E_K$ , corresponding to  $\overline{E}_D$  is given by Planck's equation for functional groups:

$$\overline{E}_{K} = \hbar \omega = \hbar \sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{0}R^{3}}}$$

$$m_{e}$$
(15.48)

The Doppler energy of the electrons of the reentrant orbit is

$$\overline{E}_{D} \cong E_{h\nu} \sqrt{\frac{2\overline{E}_{K}}{m_{e}c^{2}}} = E_{h\nu} \sqrt{\frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{0}R^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}}$$

$$(15.49)$$

 $\overline{E}_{osc}$  given by the sum of  $\overline{E}_{D}$  and  $\overline{E}_{Kvib}$  is

$$\overline{E}_{osc}(group) = n_1 \left(\overline{E}_D + \overline{E}_{Kvib}\right) = n_1 \left(E_{hv} \sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_0 R^3}}{\frac{m_e}{m_e}} + E_{vib}}\right) \tag{15.50}$$

 $E_{h\nu}$  of a group having  $n_1$  bonds is given by  $E_r$  (MO)/  $n_1$  such that

5 
$$\overline{E}_{osc} = n_1 \left( \overline{E}_D + \overline{E}_{Kvib} \right) = n_1 \left( E_T \left( \omega_0 \right) / n_1 \sqrt{\frac{2\overline{E}_K}{Mc^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$
 (15.51)

 $E_{T+osc}$  (Group) is given by the sum of  $E_T$  (MO) (Eq. (15.42)) and  $\bar{E}_{osc}$  (Eq. (15.51)):

$$E_{T+asc}$$
 (Group)=  $E_{T}$  (MO)+  $\bar{E}_{asc}$ 

$$= \left( -\frac{n_{1}e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[ c_{1}c_{2}\left(2 - \frac{a_{0}}{a}\right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \right] \right)$$

$$= \left( -\frac{n_{1}e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[ c_{1}c_{2}\left(2 - \frac{a_{0}}{a}\right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \right] \right)$$

$$+ E_{T}\left(AO / HO\right) + E_{T}\left(atom - atom, msp^{3}.AO\right)$$

$$\left[ -\frac{1}{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}}{\frac{aa_{0}}{m_{e}}} \right] + n_{1}\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

$$= \left(E(basis\ energies) + E_T\left(atom-atom, msp^3.AO\right)\right)\left[1 + \sqrt{\frac{\frac{C_{1o}C_{2o}e^2}{4\pi\varepsilon_o R^3}}{\frac{m_e}{m_e}}}\right] + n_1\frac{1}{2}\hbar\sqrt{\frac{k}{\mu}}$$

The total energy of the functional group  $E_T(group)$  is the sum of the total energy of the components comprising the energy contribution of the MO formed between the participating atoms,  $E(basis\ energies)$ , the change in the energy of the AOs or HOs upon forming the bond  $(E_T(atom-atom,msp^3.AO))$ , the energy of oscillation in the transition state, and the 5 change in magnetic energy with bond formation,  $E_{mag}$ . From Eq. (15.52), the total energy of the group  $E_T(group)$  is

$$E_{T}(Group) = \left(E(basis\ energies) + E_{T}(atom - atom, msp^{3}.AO)\right)\left[1 + \sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}} \frac{1}{m_{e}}}\right] + n_{1}\bar{E}_{Kvib} + E_{mag}$$
(15.53)

The change in magnetic energy  $E_{mag}$  which arises due to the formation of unpaired electrons in the corresponding fragments relative to the bonded group is given by

$$E_{mag} = c_3 \frac{2\pi\mu_0 e^2 \hbar^2}{m_e^2 r^3} = c_3 \frac{8\pi\mu_0 \mu_B^2}{r^3}$$
 (15.54)

where  $r^3$  is the radius of the atom that reacts to form the bond and  $c_3$  is the number of electron pairs.

$$E_{T}(Group) = \left(E(basis\ energies) + E_{T}(atom - atom, msp^{3}.AO)\right)\left[1 + \sqrt{\frac{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}{\frac{m_{e}}{m_{e}c^{2}}}}\right] + n_{1}\overline{E}_{Kvib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}}$$

$$(15.55)$$

The total bond energy of the group  $E_D$  ( $c_{roup}$ ) is the negative difference of the total energy of the group (Eq. (15.55)) and the total energy of the starting species given by the sum of  $c_4 E_{initial}$  ( $c_4 AO/HO$ ) and  $c_5 E_{initial}$  ( $c_5 AO/HO$ ):

$$E_{D}(Group) = -\left(E(basis\ energies) + E_{T}\left(atom - atom, msp^{3}.AO\right)\left[1 + \sqrt{\frac{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}{\frac{m_{e}}{m_{e}c^{2}}}}\right]\right) + n_{1}\bar{E}_{Kvib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r_{n}^{3}} - \left(c_{4}E_{Initial}\left(AO/HO\right) + c_{5}E_{Initial}\left(c_{5}AO/HO\right)\right)$$

$$(15.56)$$

In the case of organic molecules, the atoms of the functional groups are energy matched to the  $C2sp^3$  HO such that

$$E(AO/HO) = -14.63489 eV (15.57)$$

5 For examples of  $E_{mag}$  from previous sections:

$$E_{mag}\left(C2sp^{3}\right) = c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}} = c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{\left(0.91771a_{0}\right)^{3}} = c_{3}0.14803 \ eV$$
 (15.58)

$$E_{mag}\left(O2p\right) = c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} = c_3 \frac{8\pi\mu_o \mu_B^2}{a_0^3} = c_3 0.11441 \ eV \tag{15.59}$$

$$E_{mag}(N2p) = c_3 \frac{8\pi\mu_o \mu_B^2}{r^3} = c_3 \frac{8\pi\mu_o \mu_B^2}{\left(0.93084a_0\right)^3} = c_3 0.14185 \, eV$$
 (15.60)

In the general case of the solution of an organic functional group, the geometric bond parameters are solved from the semimajor axis and the relationships between the parameters by first using Eq. (15.42) to arrive at a. Then, the remaining parameters are determined using Eqs. (15.1-15.5). Next, the energies are given by Eqs. (15.52-15.59). To meet the equipotential condition for the union of the  $H_2$ -type-ellipsoidal-MO and the HO or AO of the atom of a functional group, the factor  $c_2$  of a  $H_2$ -type ellipsoidal MO in principal Eqs. (15.42) and (15.52) may given by

(i) one: 
$$c_2 = 1$$
 (15.61)

20 (ii) the ratio that is less than one of  $13.605804 \, eV$ , the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), and the magnitude of the

Coulombic energy of the participating AO or HO of the atom,  $E_{Coulomb}$  (MO.atom, msp<sup>3</sup>) given by Eqs. (15.19) and (15.31-15.32). For  $\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right>$ 13.605804 eV:

$$c_{2} = \frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-B\ AorBsp^{3}}}} = \frac{13.605804\ eV}{\left|E_{Coulomb}\left(MO.atom, msp^{3}\right)\right|}$$
(15.62)

For  $\left| E_{Coulomb} \left( MO.atom, msp^3 \right) \right| < 13.605804 \ eV$ :

$$c_2 = \frac{\frac{e^2}{8\pi\varepsilon_0 r_{A-B \land orBsp^3}}}{\frac{e^2}{8\pi\varepsilon_0 a_0}} = \frac{\left|E_{Coulomb}\left(MO.atom, msp^3\right)\right|}{13.605804 \ eV}$$
(15.63)

(iii) the ratio that is less than one of 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), and the magnitude of the valence energy, E(valence), of the participating AO or HO of the atom where E(valence) is 10 the ionization energy or  $E(MO.atom, msp^3)$  given by Eqs. (15.20) and (15.31-15.32). For  $|E(valence)| > 13.605804 \ eV$ :

$$c_{2} = \frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-B\ AorBsp^{3}}}} = \frac{13.605804\ eV}{|E(valence)|}$$
(15.64)

For |E(valence)| < 13.605804 eV:

$$c_2 = \frac{\frac{e^2}{8\pi\varepsilon_0 r_{A-B AorBsp^3}}}{\frac{e^2}{8\pi\varepsilon_0 a_0}} = \frac{|E(valence)|}{13.605804 \ eV}$$
(15.65)

15

5

(iv) the ratio that is less than one of the magnitude of the Coulombic energy of the participating AO or HO of a first atom,  $E_{Coulomb}$  (MO.atom, msp<sup>3</sup>) given by Eqs. (15.19) and (15.31-15.32), and the magnitude of the valence energy, E(valence), of the participating AO or HO of a second atom to which the first is energy matched where E(valence) is the

ionization energy or  $E(MO.atom, msp^3)$  given by Eqs. (15.20) and (15.31-15.32). For  $|E_{Conlomb}(MO.atom, msp^3)\rangle > E(valence)$ :

$$c_2 = \frac{|E(valence)|}{|E_{Coulomb}(MO.atom, msp^3)|}$$
(15.66)

For  $|E_{Coulomb}(MO.atom, msp^3)| < E(valence)$ :

$$c_2 = \frac{\left| E_{Coulomb} \left( MO.atom, msp^3 \right) \right|}{\left| E(valence) \right|}$$
 (15.67)

(v) the ratio that is less than one of the magnitude of the valence-level energies,  $E_n(valence)$ , of the AO or HO of the nth participating atom of two that are energy matched where E(valence) is the ionization energy or  $E(MO.atom, msp^3)$  given by Eqs. (15.20) and 10 (15.31-15.32):

$$c_2 = \frac{E_1(valence)}{E_2(valence)} \tag{15.68}$$

(vi) the factor that is the ratio of the hybridization factor  $c_2(1)$  of the valence AO or HO of a first atom and the hybridization factor  $c_2(2)$  of the valence AO or HO of a second atom to which the first is energy matched where  $c_2(n)$  is given by Eqs. (15.62-15.68); alternatively  $c_2$  is the hybridization factor  $c_2(1)$  of the valence AOs or HOs a first pair of atoms and the hybridization factor  $c_2(2)$  of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = \frac{c_2(1)}{c_2(2)} \tag{15.69}$$

20

(vii) the factor that is the product of the hybridization factor  $c_2(1)$  of the valence AO or HO of a first atom and the hybridization factor  $c_2(2)$  of the valence AO or HO of a second atom to which the first is energy matched where  $c_2(n)$  is given by Eqs. (15.62-15.69);

alternatively  $c_2$  is the hybridization factor  $c_2(1)$  of the valence AOs or HOs a first pair of atoms and the hybridization factor  $c_2(2)$  of the valence AO or HO a third atom or second pair to which the first two are energy matched:

$$c_2 = c_2(1)c_2(2) (15.70)$$

5 The hybridization factor  $c_2$  corresponds to the force constant k (Eqs. (11.65) and (13.58)). In the case that the valence or Coulombic energy of the AO or HO is less than 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243), then  $C_2$  corresponding to k' (Eq. (15.1)) is given by Eqs. (15.62-15.70).

Specific examples of the factors  $c_2$  and  $C_2$  of a  $H_2$ -type ellipsoidal MO of Eq. 10 (15.51) given in following sections are

$$c_{2}(C2sp^{3}HO \text{ to } F) = \frac{E(C,2sp^{3})}{E(F)}c_{2}(C2sp^{3}HO) = \frac{-14.63489 \text{ eV}}{-17.42282 \text{ eV}}(0.91771) = 0.77087;$$

$$C_{2}(C2sp^{3}HO \text{ to } Cl) = \frac{E(Cl)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-12.96764 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.81317;$$

$$C_{2}(C2sp^{3}HO \text{ to } Br) = \frac{E(Br)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-11.81381 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.74081;$$

$$C_{2}(C2sp^{3}HO \text{ to } l) = \frac{E(l)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-10.45126 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.65537;$$

$$15 \quad c_{2}(C2sp^{3}HO \text{ to } O) = \frac{E(O)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-13.61806 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.85395;$$

$$c_{2}(H \text{ to } 1^{\circ}N) = \frac{E(N)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.91140;$$

$$c_{2}(H \text{ to } 2^{\circ}N) = \frac{E(N)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.91140;$$

$$c_{2}(H \text{ to } 2^{\circ}N) = \frac{E(N)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.91140;$$

$$c_{2}(S3p \text{ to } H) = \frac{E(S,3p)}{E(H)} = \frac{-10.36001 \text{ eV}}{-13.60580 \text{ eV}} = 0.76144;$$

$$20 \quad C_{2}(C2sp^{3}HO \text{ to } S) = \frac{E(S)}{E(C,2sp^{3})}c_{2}(C2sp^{3}HO) = \frac{-10.36001 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.64965;$$

$$c_2(O \text{ to } S3sp^3 \text{ to } C2sp^3HO) = \frac{E(O)}{E(S)}c_2(C2sp^3HO)$$

$$= \frac{-13.61806 \text{ eV}}{-10.36001 \text{ eV}}(0.91771);$$

$$= 1.20632$$

$$c_2(S3sp^3) = \frac{E_{Coulomb}(S3sp^3)}{E(H)} = \frac{-11.57099 \ eV}{-13.60580 \ eV} = 0.85045;$$

$$C_2(C2sp^3HO\ to\ S3sp^3) = \frac{E(S3sp^3)}{E(C,2sp^3)}c_2(S3sp^3) = \frac{-11.52126\ eV}{-14.63489\ eV}(0.85045) = 0.66951;$$

$$C_{2}(S3sp^{3} \text{ to O to } C2sp^{3}HO) = \frac{E(S,3sp^{3})}{E(O,2p)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-11.52126 \text{ eV}}{-13.61806 \text{ eV}}(0.91771);$$

$$= 0.77641$$

$$c_{2}(O \text{ to } N2p \text{ to } C2sp^{3}HO) = \frac{E(O)}{E(N)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-14.53414 \text{ eV}}(0.91771);$$

$$= 0.85987$$

$$c_2(N2p \text{ to } O2p) = \frac{c_2(C2sp^3HO \text{ to } N)}{c_2(C2sp^3HO \text{ to } O)} = \frac{0.91140}{0.85395} = 1.06727;$$

$$C_2$$
 (benzeneC2sp<sup>3</sup>HO)= $c_2$  (benzeneC2sp<sup>3</sup>HO)= $\frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252;$ 

$$c_{2}(arylC2sp^{3}HO \ to \ O) = \frac{E(O)}{E(C,2sp^{3})}c_{2}(arylC2sp^{3}HO)$$

$$= \frac{-13.61806 \ eV}{-14.63489 \ eV}(0.85252) ;$$

$$= 0.79329$$

$$c_2(H \text{ to anline } N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.76868 \text{ eV}} = 0.92171;$$

$$c_{2}(arylC2sp^{3}HO \text{ to } N) = \frac{E(N)}{E(C,2sp^{3})}c_{2}(arylC2sp^{3}HO)$$

$$= \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}}(0.85252) ,$$

$$= 0.84665$$

and

10

5

$$C_2\left(S3p \text{ to aryl-type } C2sp^3HO\right) = \frac{E\left(S,3p\right)}{E\left(C,2sp^3\right)} = \frac{-10.36001 \text{ eV}}{-15.76868 \text{ eV}} = 0.65700.$$

## MO INTERCEPT ANGLES AND DISTANCES

Consider the general case of Eqs. (13.84-13.95) wherein the nucleus of a B atom and the 5 nucleus of a A atom comprise the foci of each  $H_2$ -type ellipsoidal MO of an A-B bond. The parameters of the point of intersection of each  $H_2$ -type ellipsoidal MO and the A-atom AO are determined from the polar equation of the ellipse:

$$r = r_0 \frac{1+e}{1+e\cos\theta'} \tag{15.71}$$

The radius of the A shell is  $r_A$ , and the polar radial coordinate of the ellipse and the radius of the A shell are equal at the point of intersection such that

$$r_{\lambda} = \left(a - c'\right) \frac{1 + \frac{c'}{a}}{1 + \frac{c'}{a}\cos\theta'}$$

$$(15.72)$$

The polar angle  $\theta'$  at the intersection point is given by

$$\theta' = \cos^{-1} \left( \frac{a}{c'} \left( (a - c') \frac{1 + \frac{c'}{a}}{a_0} - 1 \right) \right)$$
 (15.73)

Then, the angle  $\theta_{AAO}$  the radial vector of the A AO makes with the internuclear axis is

$$\theta_{AAO} = 180^{\circ} - \theta' \tag{15.74}$$

The distance from the point of intersection of the orbitals to the internuclear axis must be the same for both component orbitals such that the angle  $\omega t = \theta_{H_2MO}$  between the internuclear axis and the point of intersection of each  $H_2$ -type ellipsoidal MO with the A radial vector obeys the following relationship:

$$r_A \sin \theta_{AAO} = b \sin \theta_{H_2MO} \tag{15.75}$$

such that

$$\theta_{H_2MO} = \sin^{-1} \frac{r_a \sin \theta_{AMO}}{h} \tag{15.76}$$

The distance  $d_{H_2MO}$  along the internuclear axis from the origin of  $H_2$ -type ellipsoidal MO to the point of intersection of the orbitals is given by

$$d_{H,MO} = a\cos\theta_{H,MO} \tag{15.77}$$

The distance  $d_{AAO}$  along the internuclear axis from the origin of the A atom to the point of 5 intersection of the orbitals is given by

$$d_{AAO} = c' - d_{H,MO} (15.78)$$

## **BOND ANGLES**

Further consider an ACB MO comprising a linear combination of C-A-bond and C-B10 bond MOs where C is the general central atom. A bond is also possible between the A and B atoms of the C-A and C-B bonds. Such A-B bonding would decrease the C-A and C-B bond strengths since electron density would be shifted from the latter bonds to the former bond. Thus, the  $\angle ACB$  bond angle is determined by the condition that the total energy of the  $H_2$ -type ellipsoidal MO between the terminal A and B atoms is zero. The force constant k' of a  $H_2$ -type ellipsoidal MO due to the equivalent of two point charges of at the foci is given by:

$$k' = \frac{C_1 C_2 2e^2}{4\pi\varepsilon_0} \tag{15.79}$$

where  $C_1$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of a chemical bond of the molecule which is 0.75 (Eq. (13.59)) for a terminal A - H (A is H or other atom) and 1 20 otherwise and  $C_2$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the chemical bond and is equal to the corresponding factor of Eqs. (15.42) and (15.52). The distance from the origin of the MO to each focus c' of the A - B ellipsoidal MO is given by:

$$c' = a \sqrt{\frac{\hbar^2 4\pi \varepsilon_0}{m_e e^2 2C_1 C_2 a}} = \sqrt{\frac{aa_0}{2C_1 C_2}}$$
 (15.80)

25 The internuclear distance is

$$2c' = 2\sqrt{\frac{aa_0}{2C_1C_2}} \tag{15.81}$$

The length of the semiminor axis of the prolate spheroidal A - B MO b = c is given by Eq. (15.4).

The component energies and the total energy,  $E_T(n,MO)$ , of the A-B bond are given by the energy equations (Eqs. (11.207-11.212), (11.213-11.217), and (11.239)) of  $H_2$  except 5 that the terms based on charge are multiplied by  $c_{BO}$ , the bond-order factor which is 1 for a single bond and when the MO comprises  $n_1$  equivalent single bonds as in the case of functional groups.  $c_{BO}$  is 4 for an independent double bond as in the case of the  $CO_2$  and  $NO_2$  molecules. The kinetic energy term is multiplied by  $c'_{BO}$  which is 1 for a single bond, 2 for a double bond, and 9/2 for a triple bond. The electron energy terms are multiplied by  $c_1$ , 10 the fraction of the  $H_2$ -type ellipsoidal MO basis function of a terminal chemical bond which is 0.75 (Eq. (13.233)) for a terminal A-H (A is H or other atom) and 1 otherwise. The electron energy terms are further multiplied by  $c'_2$ , the hybridization or energy-matching factor that results in an equipotential energy match of the participating at least two atomic orbitals of each terminal bond. Furthermore, when A-B comprises atoms other than H, 15  $E_T$  (atom – atom, msp<sup>3</sup>.AO), the energy component due to the AO or HO's charge donation to the terminal MO, is added to the other energy terms to give  $E_T$  ( $\mu$ ,MO):

$$E_{T}(H_{2}MO) = \frac{-e^{2}}{8\pi\varepsilon_{0}c'} \left[ c_{1}c'_{2} \left( 2c_{BO} - c'_{BO} \frac{a_{0}}{a} \right) \ln \frac{a+c'}{a-c'} - 1 \right] + E_{T} \left( atom - atom, msp^{3}.AO \right)$$
(15.82)

The radiation reaction force in the case of the vibration of A-B in the transition state 20 corresponds to the Doppler energy,  $E_D$ , given by Eq. (11.181) that is dependent on the motion of the electrons and the nuclei. The total energy that includes the radiation reaction of the A-B MO is given by the sum of  $E_T(u_2MO)$  (Eq. (15.82)) and  $\overline{E}_{osc}$  given Eqs. (11.213-11.220), (11.231-11.236), and (11.239-11.240). Thus, the total energy  $E_T(A-B)$  of the A-B MO including the Doppler term is

$$E_{T}(A-B) = \begin{bmatrix} \left(\frac{-e^{2}}{8\pi\varepsilon_{0}c'}\left[c_{1}c'_{2}\left(2c_{BO}-c'_{BO}\frac{a_{0}}{a}\right)\ln\frac{a+c'}{a-c'}-1\right] + E_{T}\left(atom-atom,msp^{3}.AO\right) \right] \\ \left[1+\sqrt{\frac{2\hbar\sqrt{\frac{c_{BO}\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}a^{3}}}}{\frac{m_{e}}{m_{e}c^{2}}}}\right] + \frac{1}{2}\hbar\sqrt{\frac{c_{BO}\frac{c_{1}c'_{2}e^{2}}{8\pi\varepsilon_{o}a^{3}} - \frac{c_{BO}e^{2}}{8\pi\varepsilon_{o}(a+c')^{3}}}{\mu}} \\ (15.83)$$

where  $C_{1o}$  is the fraction of the  $H_2$ -type ellipsoidal MO basis function of the oscillatory transition state of the A-B bond which is 0.75 (Eq. (13.233)) in the case of H bonding to a central atom and 1 otherwise,  $C_{2o}$  is the factor that results in an equipotential energy match of the participating at least two atomic orbitals of the transition state of the chemical bond, and  $\mu = \frac{m_1 m_2}{m_1 + m_2}$  is the reduced mass of the nuclei given by Eq. (11.154). To match the boundary condition that the total energy of the A-B ellipsoidal MO is zero,  $E_T(A-B)$  given by Eq. (15.83) is set equal to zero. Substitution of Eq. (15.81) into Eq. (15.83) gives

$$10 \quad 0 = \begin{bmatrix} \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[ c_{1}c_{2}'\left(2c_{BO} - c_{BO}'\frac{a_{0}}{a}\right) \ln \frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1 \right] + E_{T}\left(atom - atom, msp^{3}.AO\right) \end{bmatrix}$$

$$\left[ \frac{1}{1 + \sqrt{\frac{2\hbar\sqrt{\frac{c_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}a^{3}}}}{m_{e}}}} + \frac{1}{2}\hbar\sqrt{\frac{c_{BO}\frac{c_{1}c_{2}'e^{2}}{8\pi\varepsilon_{o}a^{3}} - \frac{c_{BO}e^{2}}{8\pi\varepsilon_{o}}\left(a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}\right)^{3}}}{\mu}} \right]$$

$$(15.84)$$

The vibrational energy-term of Eq. (15.84) is determined by the forces between the central field and the electrons and those between the nuclei (Eqs. (11.141-11.145)). The electron-central-field force and its derivative are given by

15 
$$f(a) = -c_{BO} \frac{c_1 c_2' e^2}{4\pi \varepsilon_0 a^3}$$
 (15.85)

and

$$f'(a) = 2c_{BO} \frac{c_1 c_2' e^2}{4\pi\varepsilon_0 a^3}$$
 (15.86)

The nuclear repulsion force and its derivative are given by

$$f\left(a+c'\right) = \frac{e^2}{8\pi\varepsilon_o\left(a+c'\right)^2} \tag{15.87}$$

and

$$f'(a+c') = -\frac{e^2}{4\pi\varepsilon_o(a+c')^3}$$
 (15.88)

such that the angular frequency of the oscillation is given by

$$\omega = \sqrt{\frac{\left[\frac{-3}{a}f(a) - f'(a)\right]}{\mu}} = \sqrt{\frac{k}{m_e}} = \sqrt{\frac{c_1c_2'e^2}{4\pi\varepsilon_0a^3} - \frac{e^2}{8\pi\varepsilon_0(a+c')^2}}$$
(15.89)

Since both terms of  $\overline{E}_{osc} = \overline{E}_D + \overline{E}_{Kvib}$  are small due to the large values of a and c', to very good approximation, a convenient form of Eq. (15.84) which is evaluated to determine the bond angles of functional groups is given by

$$0 = \begin{bmatrix} \frac{-e^{2}}{8\pi\varepsilon_{0}\sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} \left[c_{1}c_{2}'\left(2 - \frac{a_{0}}{a}\right)\ln\frac{a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}}{a - \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}} - 1\right] + E_{T}\left(atom - atom, msp^{3}.AO\right) \\ \left[\frac{1 + \sqrt{\frac{c_{1}e^{2}}{4\pi\varepsilon_{o}a^{3}}}}{\frac{2\hbar\sqrt{\frac{c_{1}e^{2}}{4\pi\varepsilon_{o}a^{3}}}}{m_{e}c^{2}}}\right] + \frac{1}{2}\hbar\sqrt{\frac{c_{1}e^{2}}{8\pi\varepsilon_{o}a^{3}} - \frac{e^{2}}{8\pi\varepsilon_{o}\left(a + \sqrt{\frac{aa_{0}}{2C_{1}C_{2}}}\right)}}{\mu}}$$
(15.90)

From the energy relationship given by Eq. (15.90) and the relationship between the axes given by Eqs. (15.2-15.5), the dimensions of the A-B MO can be solved. The most convenient way to solve Eq. (15.90) is by the reiterative technique using a computer.

A factor  $c_2$  of a given atom in the determination of  $c_2'$  for calculating the zero of the total A-B bond energy is typically given by Eqs. (15.62-15.65). In the case of a H-H terminal bond of an alkyl or alkenyl group,  $c_2'$  is typically the ratio of  $c_2$  of Eq. (15.62) for the H-H bond which is one and  $c_2$  of the carbon of the corresponding C-H bond:

$$c_2' = \frac{1}{c_2(C2sp^3)} = \frac{13.605804 \, eV}{E_{Coulomb} \left(C - H \, C2sp^3\right)}$$
(15.91)

In the case of the determination of the bond angle of the ACH MO comprising a linear combination of C-A-bond and C-H-bond MOs where A and C are general, C is the central atom, and  $c_2$  for an atom is given by Eqs. (15.62-15.70),  $c_2'$  of the A-H terminal bond is typically the ratio of  $c_2$  of the A atom for the A-H terminal bond and  $c_2$  of the C atom of the corresponding C-H bond:

$$c_2' = \frac{c_2(A(A-H)msp^3)}{c_2(C(C-H)(msp^3))}$$
(15.92)

In the case of the determination of the bond angle of the COH MO of an alcohol comprising a linear combination of C-O-bond and O-H-bond MOs where C, O, and H are carbon, 10 oxygen, and hydrogen, respectively,  $c'_2$  of the C-H terminal bond is typically 0.91771 since the oxygen and hydrogen atoms are at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively) that is energy matched to the  $C2sp^3$  HO.

In the determination of the hybridization factor  $c_2'$  of Eq. (15.90) from Eqs. (15.62-15.70), the Coulombic energy,  $E_{Coulomb}\left(MO.atom, msp^3\right)$ , or the energy,  $E\left(MO.atom, msp^3\right)$ , 15 the radius  $r_{A-B.AorB.p^3}$  of the A or B AO or HO of the heteroatom of the A-B terminal bond MO such as the  $C2sp^3$  HO of a terminal C-C bond is calculated using Eq. (15.32) by considering  $\sum E_{T_{mol}}\left(MO.2sp^3\right)$ , the total energy donation to each bond with which it participates in bonding as it forms the terminal bond. The Coulombic energy  $E_{Coulomb}\left(MO.atom, msp^3\right)$  of the outer electron of the  $atom\ msp^3$  shell is given by Eq. (15.19).

- In the case that during hybridization, at least one of the spin-paired AO electrons is unpaired in the hybridized orbital (HO), the energy change for the promotion to the unpaired state is the magnetic energy E(magnetic) (Eq. (15.15)) at the initial radius r of the AO electron. Then, the energy  $E(MO.atom, msp^3)$  of the outer electron of the  $atom\ msp^3$  shell is given by the sum of  $E_{Coulomb}(MO.atom, msp^3)$  and E(magnetic) (Eq. (15.20)).
- In the specific case of the terminal bonding of two carbon atoms, the  $c_2$  factor of each carbon given by Eq. (15.62) is determined using the Coulombic energy  $E_{Coulomb} \left(C C C 2 s p^3\right)$  of the outer electron of the  $C 2 s p^3$  shell given by Eq. (15.19) with the

radius  $r_{C-C\ C2sp^3}$  of each  $C2sp^3$  HO of the terminal C-C bond calculated using Eq. (15.32) by considering  $\sum E_{T_{mol}} \left( MO, 2sp^3 \right)$ , the total energy donation to each bond with which it participates in bonding as it forms the terminal bond including the contribution of the methylene energy, 0.92918 eV (Eq. (14.513)), corresponding to the terminal C-C bond. 5 The corresponding  $E_T \left( atom-atom, msp^3.AO \right)$  in Eq. (15.90) is  $E_T \left( C-C\ C2sp^3 \right) = -1.85836\ eV$ .

In the case that the terminal atoms are carbon or other heteroatoms, the terminal bond comprises a linear combination of the HOs or AOs; thus,  $c'_2$  is the average of the hybridization factors of the participating atoms corresponding to the normalized linear sum:

10 
$$c_2' = \frac{1}{2} \left( c_2' \left( atom \ 1 \right) + c_2' \left( atom \ 2 \right) \right)$$
 (15.93)

In the exemplary cases of C-C, O-O, and N-N where C is carbon:

$$c_{2}' = \frac{1}{2} \left( \frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-A_{1}AO/HO}}} + \frac{\frac{e^{2}}{8\pi\varepsilon_{0}a_{0}}}{\frac{e^{2}}{8\pi\varepsilon_{0}r_{A-A_{2}AO/HO}}} \right)$$

$$= \frac{1}{2} \left( \frac{13.605804 \ eV}{E_{Coulomb} \left( A - A.A_{1}AO/HO \right)} + \frac{13.605804 \ eV}{E_{Coulomb} \left( A - A.A_{2}AO/HO \right)} \right)$$
(15.94)

In the exemplary cases of C-N, C-O, and C-S,

$$c_2' = \frac{1}{2} \left( \frac{13.605804 \ eV}{E_{Coulomb} \left( C - B \ C2sp^3 \right)} + c_2 \left( C \ to \ B \right) \right)$$
 (15.95)

where C is carbon and  $c_2(C \text{ to } B)$  is the hybridization factor of Eqs. (15.52) and (15.84) that matches the energy of the atom B to that of the atom C in the group. For these cases, the corresponding  $E_T(atom-atom,msp^3.AO)$  term in Eq. (15.90) depends on the hybridization and bond order of the terminal atoms in the molecule, but typical values matching those used in the determination of the bond energies (Eq. (15.56)) are

20 
$$E_T(C - O C2sp^3.O2p) = -1.44915 eV;$$
  $E_T(C - O C2sp^3.O2p) = -1.65376 eV;$   $E_T(C - N C2sp^3.N2p) = -1.44915 eV;$   $E_T(C - S C2sp^3.S2p) = -0.72457 eV;$   $E_T(O - O O2p.O2p) = -1.44915 eV;$   $E_T(O - O O2p.O2p) = -1.65376 eV;$ 

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$$E_{T}(N-N N2p.N2p) = -1.44915 \ eV; \qquad E_{T}(N-O N2p.O2p) = -1.44915 \ eV;$$

$$E_{T}(F-F F2p.F2p) = -1.44915 \ eV; \qquad E_{T}(Cl-Cl \ Cl3p.Cl3p) = -0.92918 \ eV;$$

$$E_{T}(Br-Br \ Br4p.Br4p) = -0.92918 \ eV; \qquad E_{T}(I-I \ I5p.I5p) = -0.36229 \ eV;$$

$$E_{T}(C-F \ C2sp^{3}.F2p) = -1.85836 \ eV; \qquad E_{T}(C-Cl \ C2sp^{3}.Cl3p) = -0.92918 \ eV;$$

$$E_{T}(C-Br \ C2sp^{3}.Br4p) = -0.72457 \ eV; \qquad E_{T}(C-I \ C2sp^{3}.I5p) = -0.36228 \ eV, \quad \text{and}$$

$$E_{T}(O-Cl \ O2p.Cl3p) = -0.92918 \ eV.$$

In the case that the terminal bond is X-X where X is a halogen atom,  $c_1$  is one, and  $c_2'$  is the average (Eq. (15.93)) of the hybridization factors of the participating halogen atoms given by Eqs. (15.62-15.63) where  $E_{Coulomb}\left(MO.atom,msp^3\right)$  is determined using Eq. (15.32) and  $E_{Coulomb}\left(MO.atom,msp^3\right)=13.605804\ eV$  for X=I. The factor  $C_1$  of Eq. (15.90) is one for all halogen atoms. The factor  $C_2$  of fluorine is one since it is the only halogen wherein the ionization energy is greater than that 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). For each of the other halogens, Cl, Br, and I,  $C_2$  is the hybridization factor of Eq. (15.52) given by 15 Eq. (15.70) with  $c_2\left(1\right)$  being that of the halogen given by Eq. (15.68) that matches the valence energy of X ( $E_1\left(valence\right)$ ) to that of the  $C2sp^3$  HO ( $E_2\left(valence\right)=-14.63489\ eV$ , Eq. (15.25)) and to the hybridization of  $C2sp^3$  HO ( $c_2\left(2\right)=0.91771$ , Eq. (13.430)).  $E_T\left(atom-atom,msp^3.AO\right)$  of Eq. (15.90) is the maximum for the participating atoms which is  $-1.44915\ eV$ ,  $-0.92918\ eV$ ,  $-0.92918\ eV$ , and  $-0.33582\ eV$  for F, Cl, Br, and I, 20 respectively.

Consider the case that the terminal bond is C-X where C is a carbon atom and X is a halogen atom. The factors  $c_1$  and  $c_2$  of Eq. (15.90) are one for all halogen atoms. For X=F,  $c_2'$  is the average (Eq. (15.95)) of the hybridization factors of the participating carbon and F atoms where  $c_2$  for carbon is given by Eq. (15.62) and  $c_2$  for fluorine matched to 25 carbon is given by Eq. (15.70) with  $c_2(1)$  for the fluorine atom given by Eq. (15.68) that matches the valence energy of F ( $E_1(valence) = -17.42282 \, eV$ ) to that of the  $C2sp^3$  HO

 $(E_2(valence) = -14.63489 \ eV$ , Eq. (15.25)) and to the hybridization of  $C2sp^3$  HO  $(c_2(2) = 0.91771, Eq. (13.430))$ . The factor  $C_2$  of fluorine is one since it is the only halogen wherein the ionization energy is greater than that 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H given by Eq. (1.243). For each of the other halogens, Cl, Br, and I,  $c_2'$  is the hybridization factor of the participating carbon atom since the halogen atom is energy matched to the carbon atom.  $C_2$  of the terminal-atom bond matches that used to determine the energies of the corresponding C-X-bond MO. Then,  $C_2$  is the hybridization factor of Eq. (15.52) given by Eq. (15.70) with  $c_2(1)$  for the halogen atom given by Eq. (15.68) that matches the valence energy of X ( $E_1(valence)$ ) to that of the  $C2sp^3$  HO ( $E_2(valence) = -14.63489 \ eV$ , Eq. (15.25)) and to the hybridization of  $C2sp^3$  HO ( $c_2(2) = 0.91771$ , Eq. (13.430)).  $E_T(atom-atom, msp^3.AO)$  of Eq. (15.90) is the maximum for the participating atoms which is  $-1.85836 \ eV$ ,  $-0.92918 \ eV$ ,  $-0.72457 \ eV$ , and  $-0.33582 \ eV$  for F, Cl, Br, and I, respectively.

Consider the case that the terminal bond is H-X corresponding to the angle of the atoms HCX where C is a carbon atom and X is a halogen atom. The factors  $c_1$  and  $c_2$  of Eq. (15.90) are 0.75 for all halogen atoms. For X=F,  $c_2$  is given by Eq. (15.69) with  $c_2$  of the participating carbon and F atoms given by Eq. (15.62) and Eq. (15.65), respectively. The factor  $c_2$  of fluorine is one since it is the only halogen wherein the ionization energy is greater than that 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of E0 given by Eq. (1.243). For each of the other halogens, E1, E2, and E3, and E4 is also given by Eq. (15.69) with E5 of the participating carbon given by Eq. (15.62) and E5 of the participating E7 atom given by E9. In these cases, E9 is given by Eq. (15.65) for the corresponding atom E1 where E2 matches the energy of the atom E3 to that of E4.

Using the distance between the two atoms A and B of the general molecular group ACB when the total energy of the corresponding A-B MO is zero, the corresponding bond angle can be determined from the law of cosines:

$$s_1^2 + s_2^2 - 2s_1 s_2 \text{cosine } \theta = s_3^2$$
 (15.96)

With  $s_1 = 2c'_{C-A}$ , the internuclear distance of the C-A bond,  $s_2 = 2c'_{C-B}$ , the internuclear distance of each C-B bond, and  $s_3 = 2c'_{A-B}$ , the internuclear distance of the two terminal atoms, the bond angle  $\theta_{\angle ACB}$  between the C-A and C-B bonds is given by

$$(2c'_{C-A})^2 + (2c'_{C-B})^2 - 2(2c'_{C-A})(2c'_{C-B}) cosine \theta = (2c'_{A-B})^2$$
 (15.97)

$$\theta_{\angle ACB} = \cos^{-1}\left(\frac{\left(2c'_{C-A}\right)^2 + \left(2c'_{C-B}\right)^2 - \left(2c'_{A-B}\right)^2}{2\left(2c'_{C-A}\right)\left(2c'_{C-B}\right)}\right)$$
(15.98)

Consider the exemplary structure  $C_bC_a(O_a)O_b$  wherein  $C_a$  is bound to  $C_b$ ,  $O_a$ , and  $O_b$ . In the general case that the three bonds are coplanar and two of the angles are known, say  $\theta_1$  and  $\theta_2$ , then the third  $\theta_3$  can be determined geometrically:

$$\theta_3 = 360 - \theta_1 - \theta_2 \tag{15.99}$$

10 In the general case that two of the three coplanar bonds are equivalent and one of the angles is known, say  $\theta_1$ , then the second and third can be determined geometrically:

$$\theta_2 = \theta_3 = \frac{(360 - \theta_1)}{2} \tag{15.100}$$

# ANGLES AND DISTANCES FOR AN MO THAT FORMS AN ISOSCELES

#### 15 TRIANGLE

In the general case where the group comprises three A-B bonds having B as the central atom at the apex of a pyramidal structure formed by the three bonds with the A atoms at the base in the xy-plane. The  $C_{3\nu}$  axis centered on B is defined as the vertical or z-axis, and any two A-B bonds form an isosceles triangle. Then, the angle of the bonds and the distances from and along the z-axis are determined from the geometrical relationships given by Eqs. (13.412-13.416):

the distance  $d_{origin-B}$  from the origin to the nucleus of a terminal B atom is given by

$$d_{origin-B} = \frac{2c'_{B-B}}{2\sin 60^{\circ}} \tag{15.101}$$

the height along the z-axis from the origin to the A nucleus  $d_{height}$  is given by

25 
$$d_{height} = \sqrt{(2c'_{A-B})^2 - (d_{origin-B})^2}$$
, and (15.102)

the angle  $\theta_r$ , of each A-B bond from the z-axis is given by

$$\theta_{v} = \tan^{-1} \left( \frac{d_{\text{origin-B}}}{d_{\text{height}}} \right) \tag{15.103}$$

Consider the case where the central atom B is further bound to a fourth atom C and the B-C bond is along the z-axis. Then, the bond  $\theta_{\angle ABC}$  given by Eq. (14.206) is

$$\theta_{\angle ABC} = 180 - \theta_{\nu} \tag{15.104}$$

#### DIHEDRAL ANGLE

Consider the plane defined by a general ACA MO comprising a linear combination of two C-A-bond MOs where C is the central atom. The dihedral angle  $\theta_{\angle BC/ACA}$  between the 10 ACA-plane and a line defined by a third bond with C, specifically that corresponding to a C-B-bond MO, is calculated from the bond angle  $\theta_{\angle ACA}$  and the distances between the A, B, and C atoms. The distance  $d_1$  along the bisector of  $\theta_{\angle ACA}$  from C to the internuclear-distance line between A and A,  $2c'_{A-A}$ , is given by

$$d_1 = 2c'_{C-A} \cos \frac{\theta_{\angle ACA}}{2} \tag{15.105}$$

15 where  $2c'_{C-A}$  is the internuclear distance between A and C. The atoms A, A, and B define the base of a pyramid. Then, the pyramidal angle  $\theta_{\angle ABA}$  can be solved from the internuclear distances between A and A,  $2c'_{A-A}$ , and between A and B,  $2c'_{A-B}$ , using the law of cosines (Eq. (15.98)):

$$\theta_{\angle ABA} = \cos^{-1}\left(\frac{\left(2c'_{A-B}\right)^{2} + \left(2c'_{A-B}\right)^{2} - \left(2c'_{A-A}\right)^{2}}{2\left(2c'_{A-B}\right)\left(2c'_{A-B}\right)}\right)$$
(15.106)

20 Then, the distance  $d_2$  along the bisector of  $\theta_{\angle ABA}$  from B to the internuclear-distance line  $2c'_{A-A}$ , is given by

$$d_2 = 2c'_{A-B}\cos\frac{\theta_{\angle ABA}}{2} \tag{15.107}$$

The lengths  $d_1$ ,  $d_2$ , and  $2c'_{C-B}$  define a triangle wherein the angle between  $d_1$  and the internuclear distance between B and C,  $2c'_{C-B}$ , is the dihedral angle  $\theta_{\angle BCIACA}$  that can be solved using the law of cosines (Eq. (15.98)):

$$\theta_{\angle BC/ACA} = \cos^{-1} \left( \frac{d_1^2 + (2c'_{C-B})^2 - d_2^2}{2d_1(2c'_{B-C})} \right)$$
(15.108)

## SOLUTION OF GEOMETRICAL AND ENERGY PARAMETERS OF MAJOR FUNCTIONAL GROUPS AND CORRESPONDING ORGANIC 5 MOLECULES

The exemplary molecules given in the following sections were solved using the solutions of organic chemical functional groups as basis elements wherein the structures and energies where linearly added to achieve the molecular solutions. Each functional group can be treated as a building block to form any desired molecular solution from the corresponding linear combination. Each functional group element was solved using the atomic orbital and hybrid orbital spherical orbitsphere solutions bridged by molecular orbitals comprised of the  $H_2$ -type prolate spheroidal solution given in the Nature of the Chemical Bond of Hydrogen-Type Molecules section. The energy of each MO was matched at the HO or AO by matching the hybridization and total energy of the MO to the AOs and HOs. The energy  $E_{mag}$  (e.g. given 15 by Eq. (15.58)) for a  $C2sp^3$  HO and Eq.(15.59) for an O2p AO) was subtracted for each set

The bond energy is not equal to the component energy of each bond as it exists in the molecule; although, they are close. The total energy of each group is its contribution to the total energy of the molecule as a whole. The determination of the bond energies for the creation of the separate parts must take into account the energy of the formation of any radicals and any redistribution of charge density within the pieces and the corresponding energy change with bond cleavage. Also, the vibrational energy in the transition state is dependent on the other groups that are bound to a given functional group. This will effect the functional-group energy. But, because the variations in the energy based on the balance of the molecular composition are typically of the order of a few hundreds of electron volts at most, they were neglected.

of unpaired electrons created by bond breakage.

The energy of each functional-group MO bonding to a given carbon HO is independently matched to the HO by subtracting the contribution to the change in the energy of the HO from the total MO energy given by the sum of the MO contributions and  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (13.428)). The intercept angles are determined from Eqs.

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(15.71-15.78) using the final radius of the HO of each atom. The final carbon-atom radius is determined using Eqs. (15.32) wherein the sum of the energy contributions of each atom to all the MOs in which it participates in bonding is determined. This final radius is used in Eqs. (15.19) and (15.20) to calculate the final valence energy of the HO of each atom at the corresponding final radius. The radius of any bonding heteroatom that contributes to a MO is calculated in the same manner, and the energy of its outermost shell is matched to that of the MO by the hybridization factor between the carbon-HO energy and the energy of the heteroatomic shell. The donation of electron density to the AOs and HOs reduces the energy. The donation of the electron density to the MO's at each AO or HO is that which causes the resulting energy to be divided equally between the participating AOs or HOs to achieve energy matching.

The molecular solutions can be used to design synthetic pathways and predict product yields based on equilibrium constants calculated from the heats of formation. New stable compositions of matter can be predicted as well as the structures of combinatorial chemistry reactions. Further important pharmaceutical applications include the ability to graphically or computationally render the structures of drugs that permit the identification of the biologically active parts of the molecules to be identified from the common spatial charge-density functions of a series of active molecules. Drugs can be designed according to geometrical parameters and bonding interactions with the data of the structure of the active site of the 20 drug.

To calculate conformations, folding, and physical properties, the exact solutions of the charge distributions in any given molecule are used to calculate the fields, and from the fields, the interactions between groups of the same molecule or between groups on different molecules are calculated wherein the interactions are distance and relative orientation dependent. The fields and interactions can be determined using a finite-element-analysis approach of Maxwell's equations.

### AROMATIC AND HETEROCYCLIC COMPOUNDS

Aromatic and heterocyclic molecules comprise at least one of an aromatic or a cyclic conjugated alkene functional group. The latter was described in the Cyclic and Conjugated Alkenes section. The aromatic bond is uniquely stable and requires the sharing of the electrons of multiple  $H_2$ -type MOs. The results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule  $(C_6H_6)$  section can be generalized to any aromatic function group(s) of aromatic and heterocyclic compounds.

 $C_6H_6$  can be considered a linear combination of three ethylene molecules wherein a C-H bond of each  $CH_2$  group of  $H_2C=CH_2$  is replaced by a C=C bond to form a six-10 member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule  $(CH_2CH_2)$  section. The radius  $r_{ethylene2sp}$ ,  $(0.85252a_0)$  of the  $C2sp^3$  shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy  $E_{Coulomb}(C_{ethylene}, 2sp^3)$  (-15.95955 eV) of the outer electron of the  $C2sp^3$  shell is given by Eq. (14.245). The energy  $E(C_{ethylene}, 2sp^3)$  (-15.76868 eV) of the outer electron of the  $C2sp^3$  shell 15 is given by Eq. (14.246).  $E_T(C=C,2sp^3)$  (-1.13380 eV) (Eq. (14.247), the energy change of each  $C2sp^3$  shell with the formation of the C = C-bond MO is given by the difference between  $E(C_{ethvlene}, 2sp^3)$  and  $E(C, 2sp^3)$ .  $C_6H_6$  can be solved using the same principles as those used to solve ethylene wherein the 2s and 2p shells of each C hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  hybridized orbitals 20 (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each  $2sp^3$  HO of each carbon atom initially has four unpaired electrons. Thus, the 6H atomic orbitals (AOs) of benzene contribute six electrons and the six  $sp^3$ -hybridized carbon atoms contribute twenty-four electrons to form six C-H bonds and six C = C bonds. Each C - H bond has two paired electrons with one donated from the H AO 25 and the other from the  $C2sp^3$  HO. Each C=C bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two C2sp3 HOs of the participating carbon atoms. Each C-H and each C=C bond comprises a linear combination of one and two diatomic  $H_2$ -type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively. 30

Consider the case where three sets of C = C-bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two  $C2sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the  $C2sp^3$  HOs:

35 
$$\begin{cases} 3(2 C2sp^3 + 0.75 H_2 MO) \rightarrow 3(C=C) - ethylene - type - bond MO \\ \rightarrow 6(C=C) - bond MO of benzene \end{cases}$$
 (15.142)

The linear combination of each  $H_2$ -type ellipsoidal MO with each  $C2sp^3$  HO further comprises an excess 25% charge-density contribution per bond from each  $C2sp^3$  HO to the C=C-bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond C=C-bond are determined using Eqs. (15.42) and (15.1-15.5) in a form that are the same equations as those used to determine the same parameters of the C=C-bond MO of ethylene (Eqs. (14.242-14.268)) while matching the boundary conditions of the structure of benzene.

Hybridization with 25% electron donation to each C = C-bond gives rise to the  $C_{benzene} 2sp^3$  HO-shell Coulombic energy  $E_{Coulomb} \left( C_{benzene}, 2sp^3 \right)$  given by Eq. (14.245). To meet the equipotential condition of the union of the six  $C2sp^3$  HOs,  $c_2$  and  $c_3$  of Eq. (15.42) for the

aromatic C=C-bond MO is given by Eq. (15.62) as the ratio of 15.95955 eV, the magnitude of  $E_{Coulomb}\left(C_{benzene}, 2sp^3\right)$  (Eq. (14.245)), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of H (Eq. (1.243)):

$$C_2$$
 (benzeneC2sp<sup>3</sup>HO)= $c_2$  (benzeneC2sp<sup>3</sup>HO)= $\frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252$  (15.143)

The energies of each C=C bond of benzene are also determined using the same equations as those of ethylene (Eqs. (14.251-14.253) and (14.319-14.333) with the parameters of benzene. Ethylene serves as a basis element for the C=C bonding of benzene wherein each of the six C=C bonds of benzene comprises (0.75)(4)=3 electrons according to Eq. (15.142). The total energy of the bonds of the eighteen electrons of the C=C bonds of benzene,  $E_T\left(C_6H_6, C=C\right)$ , is given by (6)(0.75) times  $E_{T+osc}(C=C)$  (Eq. (14.492)), the total energy of the C=C-bond MO of benzene including the Doppler term, minus eighteen times  $E(C,2sp^3)$  (Eq. (14.146)), the initial energy of each  $C2sp^3$  HO of each C that forms the C=C bonds of bond order two. Thus, the total energy of the six C=C bonds of benzene with three electron per aromatic bond given by Eq. (14.493) is

$$E_{T}\left(C_{6}H_{6},C=C\right) = (6)(0.75)E_{T+osc}\left(C=C\right) - (6)(3)E\left(C,2sp^{3}\right)$$

$$= (6)(0.75)\left(-66.05796 \ eV\right) - 18\left(-14.63489 \ eV\right)$$

$$= -297.26081 \ eV - \left(-263.42798 \ eV\right)$$

$$= -33.83284 \ eV$$
(15.144)

25 The results of benzene can be generalized to the class of aromatic and heterocyclic compounds.  $E_{hr}$  of an aromatic bond is given by  $E_{T}(H_{2})$  (Eqs. (11.212) and (14.486)), the maximum total energy of each  $H_{2}$ -type MO such that

$$\bar{E}_{osc} = n_1 \left( \bar{E}_D + \bar{E}_{Kvib} \right) = n_1 \left( -31.63536831 \ eV \sqrt{\frac{2\bar{E}_K}{Mc^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$
 (15.145)

The factor of 0.75 corresponding to the three electrons per aromatic bond of bond order two 30 given in the Benzene Molecule ( $C_6H_6$ ) section modifies Eqs. (15.52-15.56). Multiplication of

the total energy given by Eq. (15.55) by  $f_1 = 0.75$  with the substitution of Eq. (15.145) gives the total energy of the aromatic bond:

$$E_{T}(Group) = f_{1} \left( E(basis\ energies) + E_{T}(atom - atom, msp^{3}.AO) - 31.63536831\ eV \sqrt{\frac{\sum_{1o}^{C_{1o}C_{2o}e^{2}} \frac{4\pi\varepsilon_{o}R^{3}}{m_{e}}}{m_{e}c^{2}} + n_{1}\bar{E}_{Kvib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}}} \right)$$
(15.146)

5 The total bond energy of the aromatic group  $E_D$  (Group) is the negative difference of the total energy of the group (Eq. (15.146)) and the total energy of the starting species given by the sum of  $c_4 E_{initial}$  ( $c_4 AO/HO$ ) and  $c_5 E_{initial}$  ( $c_5 AO/HO$ ):

$$E_{D}(Group) = -\left( \int_{1}^{1} \left( E(basis\ energies) + E_{T}(atom - atom, msp^{3}.AO) \right) - \left( \int_{1}^{1} \left( \frac{E(basis\ energies) + E_{T}(atom - atom, msp^{3}.AO)}{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}} \right) - \left( \frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\varepsilon_{o}R^{3}}}}{m_{e}} + n_{1}\bar{E}_{Kvib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}} \right) - \left( c_{4}E_{intital}(AO/HO) + c_{5}E_{muttal}(c_{5}AO/HO) \right)$$
(15.147)

Since there are three electrons per aromatic bond,  $c_4$  is three times the number of aromatic 10 bonds.

Benzene can also be considered as comprising chemical bonds between six CH radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of CH is given in the Hydrogen Carbide (CH) section. Those of the benzene are given in the Benzene Molecule  $(C_6H_6)$  section. The energy components of  $V_e$ ,  $V_p$ ,

15 T,  $V_m$ , and  $E_T$  are the same as those of the hydrogen carbide radical, except that  $E_T\left(C=C,2sp^3\right)=-1.13379~eV$  (Eq. (14.247)) is subtracted from  $E_T\left(CH\right)$  of Eq. (13.495) to match the energy of each C-H-bond MO to the decrease in the energy of the corresponding  $C2sp^3$  HO. In the corresponding generalization of the aromatic CH group, the geometrical parameters are determined using Eq. (15.42) and Eqs. (15.1-15.5) with  $E_T\left(atom-atom,msp^3.AO\right)=-1.13379~eV$ .

The total energy of the benzene C-H-bond MO,  $E_{T_{burner}}\left(C-H\right)$ , given by Eq. (14.467) is the sum of  $0.5E_{T}\left(C=C,2sp^{3}\right)$ , the energy change of each  $C2sp^{3}$  shell per single bond due to the decrease in radius with the formation of the corresponding C=C-bond MO (Eq. (14.247)), and  $E_{T_{burner}}\left(CH\right)$ , the  $\sigma$  MO contribution given by Eq. (14.441). In the corresponding 25 generalization of the aromatic CH group, the energy parameters are determined using Eqs. (15.146-15.147) with  $f_{1}=1$  and  $E_{T}\left(atom-atom,msp^{3}.AO\right)=\frac{-1.13379\ eV}{2}$ . Thus, the energy

contribution to the single aromatic CH bond is one half that of the C=C double bond contribution. This matches the energies of the CH and C=C aromatic groups, conserves the electron number with the equivalent charge density as that of s=1 in Eqs. (15.18-15.21), and further gives a minimum energy for the molecule. Breakage of the aromatic C=C bonds to give CH groups creates unpaired electrons in these fragments that corresponds to  $c_3=1$  in Eq. (15.56) with  $E_{max}$  given by Eq. (15.58).

Each of the C-H bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each C-H bond,  $-E_{D_{benzene}}\binom{12}{C}H$  (Eq. (14.477)), the total energy of the twelve electrons of the six C-H bonds of benzene,  $E_T(C_6H_6,C-H)$ , given by Eq. (14.494) 10 is

$$E_T(C_6H_6, C-H) = (6)(-E_{D_{become}}(^{12}CH)) = 6(-3.90454 \text{ eV}) = -23.42724 \text{ eV}$$
 (15.148)

The total bond dissociation energy of benzene,  $E_D(C_6H_6)$ , given by Eq. (14.495) is the negative

sum of 
$$E_T \left( C_6 H_6, C = C \right)$$
 (Eq. (14.493)) and  $E_T \left( C_6 H_6, C - H \right)$  (Eq. (14.494)):

$$E_{D}(C_{6}H_{6}) = -\left(E_{T}(C_{6}H_{6}, C = C) + E_{T}(C_{6}H_{6}, C - H)\right)$$

$$= -\left((-33.83284 \ eV) + (-23.42724 \ eV)\right)$$

$$= 57.2601 \ eV$$
(15.149)

15 Using the parameters given in Tables 15.214 and 15.216 in the general equations (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)) reproduces the results for benzene given in the Benzene Molecule ( $C_6H_6$ ) section as shown in Tables 15.214 and 15.216.

The symbols of the functional groups of aromatics and hertocyclics are given in Table 15.213. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and 20 energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aromatics and hertocyclics are given in Tables 15.214, 15.215, and 15.216, respectively. The total energy of benzene given in Table 15.217 was calculated as the sum over the integer multiple of each  $E_D$  (Group) of Table 15.216 corresponding to functional-group composition of the molecule. The bond angle parameters of benzene determined using Eqs. (15.79-15.108) are given in Table 15.218.

Table 15.213. The symbols of functional groups of aromatics and hertocyclics.

Functional Group	Group Symbol
CC (aromatic bond)	3e C=C
CH (aromatic)	CH (i)

Table 15.214. The geometrical bond parameters of aromatics and hertocyclics and

experimental values [1].

Parameter	C = C Group	<i>CH</i> Group
$a\left(a_{_{0}}\right)$	1.47348	1.60061
$c'(a_0)$	1.31468	1.03299
Bond Length $2c'(\Box)$	1.39140	1.09327
Exp. Bond Length	1.399 (benzene)	1.101 (benzene)
$b,c$ $(a_0)$	0.66540	1.22265
е	0.89223	0.64537

5 Table 15.216. The energy parameters (eV) of functional groups of aromatics and heterocyclics.

Parameters	C = C Group	CH Group
$f_1$	0.75	1
$n_{\rm l}$	2	1
$n_2$	0	0
$n_3$	0	0
$C_1$	0.5	0.75
C <sub>2</sub>	0.85252	1
$c_{_{\mathbf{i}}}$	1	1
	0.85252	0.91771
$c_3$	0	1
C <sub>4</sub>	3	. 1
<i>c</i> <sub>5</sub>	0	1
$C_{lo}$	0.5	0.75
$C_{2o}$	0.85252	1
$V_e$ (eV)	-101.12679	-37.10024
$V_{p}$ (eV)	20.69825	13.17125
T(eV)	34.31559	11.58941
$V_{m}(eV)$	-17.15779	-5.79470
E(AOIHO)(eV)	0	-14.63489
$\Delta E_{H_2MO}$ (логно) (eV)	0	-1.13379

<del></del>	
0	-13.50110
-63.27075	-31.63539
-2.26759	-0.56690
-65.53833	-32.20226
49.7272	26.4826
32.73133	17.43132
-0.35806	-0.26130
0.19649 [49]	0.35532 Eq. (13.458)
-0.25982	-0.08364
0.14803	0.14803
-49.54347	-32.28590
-14.63489	-14.63489
0	-13.59844
5.63881	3.90454
	-63.27075 -2.26759 -65.53833 49.7272 32.73133 -0.35806 0.19649 [49] -0.25982 0.14803 -49.54347 -14.63489 0

Table 15.215. The MO to HO intercept geometrical bond parameters of benzene.  $E_r$  is  $E_r(atom-atom,msp^3.AO)$ .

-								
Bond	Atom	$E_T$	$E_{7}$	$E_{T}$	$E_{r}$	Final Total	7.	
-		(eV)	(eV)	(eV)	(eV)	Energy		janal (
	-	Bond 1	Bond 2	Bond 3	Bond 4	$C2sp^3$	(g)	$(a_0)$
Ì						(eV)		
C-H(CH)	Ö	-0.85035	-0.85035	-0.56690	. 0	-153.88327	0.91771	0.79597
30 20		0.0000	20000					
C = HC = C	ゔ゚	-0.62033	-0.85035	-0.56690	0	-153.88327	0.91771	0.79597
200					•			
						T		

-					•		
Bond	$E_{Coulomb}(C2sp^3)(eV)$	$E(C2sp^3)$	ι,θ	$\theta_1$	$\theta_{_{2}}$	d,	ď,
	Final (eV) Final	(eV) Final	<u></u>	<u></u>	©	$\begin{pmatrix} a_o \end{pmatrix}$	$(a_0)$
C-H(CH)	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0.21379
$C = HC_a = C$	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533

Table 15.217. The total bond energies of benzene calculated using the functional group composition and the energies of Table 15.216 compared to the experimental values [2].

Relative Error	0.00006
Experimental Total Bond Energy (eV)	57.26340
Calculated Total Bond Energy (eV)	57.26008
. НЭ	9
C = C	9
Name	Benzene
Fornula	CcH

Table 15.218. The bond angle parameters of benzene and experimental values [1].  $E_T$  is  $E_T(atom-atom,msp^3.AO)$ .

Atoms of	2c' Bond 1 (a <sub>0</sub> )	$2c'$ Bond 2 $(a_0)$	$2c'$ Terminal Atoms $(a_0)$	Ecoulombi Atom 1	Atom 1  Hybridization Designation (Table 15.3.A)	Coulombi Atom 2	Atom 2  Hybridization Designation (Table	C <sub>2</sub> Atom 1	C <sub>2</sub> C <sub>1</sub> C <sub>2</sub>	Ü	2
ZCCC (aromatic)	2.62936	2.62936	4.5585	2.62936 2.62936 4.5585 -17.17218		-17.17218	34	0.79232	0.79232 0.79232	1	T-
НЭЭ7											T
(aromatic)											

			7			Γ-	_	
	$\text{Exp. } \theta$	>		[2C-0C] 021	(penzene)	1.20 550 521	[40-0c] 021	(penzene)
	Cal. $\theta$	>		120.19			119.91	
	92	D						
	φ <sup>-</sup> @	$\geq$					170.19	
	<i>ه</i> ° و		:					
	$E_{\mathcal{T}}$ (eV)	,		-1.85836				
	<i>-</i> 6°		0000	0.79232				Y
	ഗ			-				
Atoms of Angle	•	2007	7777	(aromatic)	HJJ)/		(aromatic)	

Table 1.1. The calculated and experimental total bond energies of n-alkanes using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
C <sub>3</sub> H <sub>8</sub>	Propane	41.46896	41.434	-0.00085
C4H10	Butane	53.62666	53.61	-0.00036
C <sub>5</sub> H <sub>12</sub>	Pentane	65.78436	65.77	-0.00017
$C_6H_{14}$	Hexane	77.94206	77.93	-0.00019
C7H16	Heptane	90.09976	90.09	-0.00013
C <sub>8</sub> H <sub>18</sub>	Octane	102.25746	102.25	-0.00006
C <sub>9</sub> H <sub>20</sub>	Nonane	114.41516	114.40	-0.00012
$C_{10}H_{22}$	Decane	126.57286	126.57	-0.00003
$C_{11}H_{24}$	Undecane	138.73056	138.736	0.00004
$C_{12}H_{26}$	Dodecane	150.88826	150.88	-0.00008
C <sub>18</sub> H <sub>38</sub>	Octadecane	223.83446	223.85	0.00008

Table 1.2. The calculated and experimental total bond energies of branched alkanes using closed-form equations having integers and fundamental constants only.

	,		•	
•	••••	Calculated	Experimental	Relative Erro
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
C <sub>4</sub> H <sub>10</sub>	Isobutane	53.69922	53.695	-0.00007
$C_5H_{12}$	Isopentane	65.85692	65.843	-0.00021
C <sub>5</sub> H <sub>12</sub>	Neopentane	65.86336	65.992	0.00195
C <sub>6</sub> H <sub>14</sub>	2-Methylpentane	78.01462	78.007	-0.00010
C <sub>6</sub> H <sub>14</sub>	3-Methylpentane	78.01462	77.979	-0.00046
C <sub>6</sub> H <sub>14</sub>	2,2-Dimethylbutane	78.02106	78.124	0.00132
C <sub>6</sub> H <sub>14</sub>	2,3-Dimethylbutane	77.99581	78.043	0.00061
C7H16	2-Methylhexane	90.17232	90.160	-0.00014
C7H16	3-Methylhexane	90.17232	90.127	-0.00051
C <sub>7</sub> H <sub>16</sub>	3-Ethylpentane	90.17232	90.108	-0.00072
C7H16	2,2-Dimethylpentane	90.17876	90.276	0.00107
C7H16	2,2,3-Trimethylbutane	90.22301	90.262	0.00044
C <sub>7</sub> H <sub>16</sub>	2,4-Dimethylpentane	90.24488	90.233	-0.00013
C <sub>7</sub> H <sub>16</sub>	3,3-Dimethylpentane	90.17876	90.227	0.00054
C <sub>8</sub> H <sub>18</sub>	2-Methylheptane	102.33002	102.322	-0.00008
C <sub>8</sub> H <sub>i8</sub>	3-Methylheptane	102.33002	102.293	-0.00036
C <sub>8</sub> H <sub>18</sub>	4-Methylheptane	102.33002	102.286	-0.00043
C <sub>8</sub> H <sub>18</sub>	3-Ethylhexane	102.30169	102.274	-0.00027
C <sub>8</sub> H <sub>18</sub>	2,2-Dimethylhexane	102.33646	102.417	0.00079
C <sub>8</sub> H <sub>18</sub>	2,3-Dimethylhexane	102.31121	102.306	-0.00005
C <sub>8</sub> H <sub>18</sub>	2,4-Dimethylhexane	102.40258	102.362	-0.00040
C <sub>8</sub> H <sub>18</sub>	2,5-Dimethylhexane	102.40258	102.396	-0.00006
C <sub>8</sub> H <sub>18</sub>	3,3-Dimethylhexane	102.33646	102.369	0.00032
C <sub>8</sub> H <sub>18</sub>	3,4-Dimethylhexane	102.31121	102.296	-0.00015
C <sub>8</sub> H <sub>18</sub>	3-Ethyl-2-methylpentane	102.31121	102,277	-0.00033
C <sub>8</sub> H <sub>18</sub>	3-Ethyl-3-methylpentane	102.33646	102.317	-0.00019
C <sub>8</sub> H <sub>18</sub>	2,2,3-Trimethylpentane	102.38071	102.370	-0.00010
C <sub>8</sub> H <sub>18</sub>	2,2,4-Trimethylpentane	102.40902	102.412	0.00003
C <sub>8</sub> H <sub>18</sub>	2,3,3-Trimethylpentane	102.38071	102.332	-0.00048
C <sub>8</sub> H <sub>18</sub>	2,3,4-Trimethylpentane	102.29240	102.342	0.00049
C <sub>8</sub> H <sub>18</sub>	2,2,3,3-Tetramethylbutane	102.41632	102.433	0.00016
C <sub>9</sub> H <sub>20</sub>	2,3,5-Trimethylhexane	114.54147	114.551	0.00008
C <sub>9</sub> H <sub>20</sub>	3,3-Diethylpentane	114.49416	114.455	-0.00034
C <sub>9</sub> H <sub>20</sub>	2,2,3,3-Tetramethylpentane	114.57402	114.494	-0.00070
C <sub>9</sub> H <sub>20</sub>	2,2,3,4-Tetramethylpentane	. 114.51960	114.492	-0.00024

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>9</sub> H <sub>20</sub>	2,2,4,4-Tetramethylpentane	114.57316	114.541	-0.00028
$C_9H_{20}$	2,3,3,4-Tetramethylpentane	114.58266	114.484	-0.00086
$C_{10}H_{22}$	2-Methylnonane	126.64542	126,680	0.00027
C <sub>10</sub> H <sub>22</sub>	5-Methylnonane	126.64542	126.663	0.00014

Table 1.3. The calculated and experimental total bond energies of alkenes using closed-form equations having integers and fundamental constants only.

Formul-	N	Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
0.11		Energy (eV)	Energy (eV)	
C <sub>3</sub> H <sub>6</sub>	Ргореле	35.56033	35.63207	0.00201
C <sub>4</sub> H <sub>8</sub>	1-Butene	47.71803	47.78477	0.00140
C <sub>4</sub> H <sub>8</sub>	trans-2-Butene	47.93116	47.90395	-0.00057
C <sub>4</sub> H <sub>8</sub>	Isobutene	47.90314	47.96096	0.00121
C <sub>5</sub> H <sub>to</sub>	1-Pentene	59.87573	59.95094	0.00125
C <sub>5</sub> H <sub>10</sub>	trans-2-Pentene	60.08886	60.06287	-0.00043
C <sub>5</sub> H <sub>10</sub>	2-Methyl-1-butene	60.06084	. 60.09707	0.00060
C <sub>5</sub> H <sub>10</sub>	2-Methyl-2-butene	60.21433	60.16444	-0.00083
C <sub>5</sub> H <sub>10</sub>	3-Methyl-1-butene	59.97662	60.01727	0.00068
$C_6H_{12}$	1-Hexene	72.03343	72.12954	0.00133
$C_6H_{12}$	trans-2-Hexene	72.24656	72.23733	-0.00013
$C_6H_{12}$	trans-3-Hexene	72.24656	72.24251	-0.00006
C <sub>6</sub> H <sub>12</sub>	2-Methyl-1-pentene	72.21854	72.29433	0.00105
C <sub>6</sub> H <sub>12</sub>	2-Methyl-2-pentene	72.37203	72.37206	0.00000
$C_6H_{12}$	3-Methyl-1-pentene	72.13432	72.19173	0.00080
C <sub>6</sub> H <sub>12</sub>	4-Methyl-1-pentene	72.10599	72.21038	0.00145
C <sub>6</sub> H <sub>12</sub>	3-Methyl-trans-2-pentene	72,37203	72.33268	-0.00054
C <sub>6</sub> H <sub>12</sub>	4-Methyl-trans-2-pentene	72.34745	72.31610	-0.00043
C <sub>6</sub> H <sub>12</sub>	2-Ethyl-1-butene	72.21854	72.25909	0.00056
C <sub>6</sub> H <sub>12</sub>	2,3-Dimethyl-1-butene	72.31943	72.32543	0.00008
C <sub>6</sub> H <sub>12</sub>	3,3-Dimethyl-1-butene	72,31796	72.30366	-0.00020
C <sub>6</sub> H <sub>12</sub>	2,3-Dimethyl-2-butene	72.49750	72.38450	-0.00156
C <sub>7</sub> H <sub>14</sub>	1-Heptene	84.19113	84.27084	0.00095
C7H14	5-Methyl-1-hexene	84.26369	84.30608	0.00050
C7H14	trans-3-Methyl-3-hexene	84.52973	84,42112	-0.00129
C7H14	2,4-Dimethyl-1-pentene	84.44880	84.49367	0.00053
C7H14	4,4-Dimethyl-1-pentene	84.27012	84.47087	0.00238
C <sub>7</sub> H <sub>14</sub>	2,4-Dimethyl-2-pentene	84.63062	84.54445	-0.00102
C <sub>7</sub> H <sub>14</sub>	trans-4,4-Dimethyl-2-pentene	84.54076	84.54549	0.00006
C <sub>7</sub> H <sub>14</sub>	2-Ethyl-3-methyl-1-butene	84.47713	84.44910	-0.00033
C7H14	2,3,3-Trimethyl-1-butene	84.51274	84.51129	-0.00002
C <sub>8</sub> H <sub>16</sub>	1-Octene	96.34883	96.41421	0.00068
C <sub>8</sub> H <sub>16</sub>	trans-2,2-Dimethyl-3-hexene	96.69846	96.68782	-0.00011
C <sub>8</sub> H <sub>16</sub>	3-Ethyl-2-methyl-1-pentene	96.63483	96.61113	-0.00025
C <sub>8</sub> H <sub>16</sub>	2,4,4-Trimethyl-1-pentene	96.61293	96.71684	0.00107
C <sub>8</sub> H <sub>16</sub>	2,4,4-Trimethyl-2-pentene	96.67590	96.65880	-0.00018
$C_{10}H_{20}$	1-Decene	120.66423	120.74240	0.00065
$C_{12}H_{24}$	1-Dodecene	144.97963	145.07163	0.00063
$C_{16}H_{32}$	1-Hexadecene	193.61043	193.71766	0.00063

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Table 1.4. The calculated and experimental total bond energies of alkynes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>3</sub> H <sub>4</sub>	Propyne	29,42932	29.40432	-0.00085
C₄H <sub>6</sub>	1-Butyne	41.58702	41.55495	-0.00083
C <sub>4</sub> H <sub>6</sub>	2-Butyne	41.72765	41.75705	0.00070
C <sub>9</sub> H <sub>16</sub>	1-Nonyne	102.37552	102.35367	-0.00021

Table 1.5. The calculated and experimental total bond energies of alkyl fluorides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CF₄	Tetrafluoromethane Trifluoromethane Difluoromethane 1-Fluoropropane 2-Fluoropropane	21.07992	21.016	-0.00303
CHF₃		19.28398	19.362	0.00405
CH₂F₂		18.22209	18.280	0.00314
C₃H₂F		41.86745	41.885	0.00041
C₃H₂F		41.96834	41.963	-0.00012

Table 1.6. The calculated and experimental total bond energies of alkyl chlorides using closed-form equations having integers and fundamental constants only.

			omi,	
Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CCl <sub>4</sub>	Tetrachloromethane	13.43181	13.448	0.00123
CHCl₃	Trichloromethane	14.49146	14.523	0.00123
$CH_2Cl_2$	Dichloromethane	15.37248	15.450	0.00217
CH₃Ci	Chloromethane	16.26302	16.312	0.00299
C <sub>2</sub> H <sub>5</sub> Cl	Chloroethane	28.61064	28.571	-0.00233
C₃H <sub>7</sub> Cl	1-Chloropropane	40.76834	40.723	-0.00138
C <sub>3</sub> H <sub>7</sub> Cl	2-Chloropropane	40.86923	40.858	-0.00112
· C <sub>4</sub> H <sub>9</sub> Cl	1-Chlorobutane	52.92604	52.903	-0.00044
$C_4H_9Cl$	2-Chlorobutane	53.02693	52.972	
C <sub>4</sub> H <sub>9</sub> Cl	1-Chloro-2-methylpropane	52.99860	52.953	-0.00104
C <sub>4</sub> H <sub>9</sub> Cl	2-Chloro-2-methylpropane	53.21057	53.191	-0.00085
C <sub>5</sub> H <sub>11</sub> Cl	1-Chloropentane	65.08374	65.061	-0.00037
C <sub>5</sub> H <sub>11</sub> Cl	1-Chloro-3-methylbutane	65.15630	65.111	-0.00034
C <sub>5</sub> H <sub>11</sub> Cl	2-Chloro-2-methylbutane	65.36827	65.344	-0.00069
C <sub>5</sub> H <sub>11</sub> Cl	2-Chloro-3-methylbutane	65.16582		-0.00037
C <sub>6</sub> H <sub>13</sub> Cl	2-Chlorohexane	77.34233	65.167	0.00002
C <sub>8</sub> H <sub>17</sub> Cl	1-Chlorooctane		77.313	-0.00038
C <sub>12</sub> H <sub>25</sub> Cl	1-Chlorododecane	101.55684	101.564	0.00007
C <sub>18</sub> H <sub>37</sub> Cl	1-Chlorooctadecane	150.18764	150.202	0.00009
-103/01	- Chiorocoladecane	223.13384	223.175	0.00018

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Table 1.7. The calculated and experimental total bond energies of alkyl bromides using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
CBr <sub>4</sub>	Tetrabromomethane	11.25929	11.196	-0.00566
CHBr₃	Tribromomethane	12.87698	12.919	0.00323
CH₃Br	Bromomethane	15.67551	15.732	0.00360
C <sub>2</sub> H <sub>5</sub> Br	Bromoethane	28.03939	27.953	-0.00308
C <sub>3</sub> H <sub>7</sub> Br	1-Bromopropane	40.19709	40.160	-0.00093
C <sub>3</sub> H <sub>7</sub> Br	2-Bromopropane	40.29798	40.288	-0.00024
$C_5H_{10}Br_2$	2,3-Dibromo-2-methylbutane	63.48143	63.477	-0.00027
C <sub>6</sub> H <sub>13</sub> Br	1-Bromohexane	76,67019	76.634	-0.00047
C7H15Br	1-Bromoheptane	88.82789	88.783	-0.00051
C <sub>8</sub> H <sub>17</sub> Br	1-Bromooctane	100.98559	100.952	-0.00031
$C_{12}H_{25}Br$	1-Bromododecane	149.61639	149,573	-0.00033
$C_{16}H_{33}Br$	1-Bromohexadecane	198,24719	198.192	-0.00029

Table 1.8. The calculated and experimental total bond energies of alkyl iodides using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
CHl <sub>3</sub>	Triiodomethane	10.35888	10.405	0.00444
CH <sub>2</sub> I <sub>2</sub>	Diiodomethane	12.94614	12.921	-0.00195
CH <sub>3</sub> I	Iodomethane	15.20294	15.163	-0.00263
C <sub>2</sub> H <sub>5</sub> I	Iodoethane	27.36064	27.343	-0.00066
C <sub>3</sub> H <sub>7</sub> I	1-Iodopropane	39.51834	39.516	-0.00006
C <sub>3</sub> H <sub>7</sub> I	2-lodopropane	39.61923	39.623	0.00009
C <sub>4</sub> H <sub>9</sub> I	2-Iodo-2-methylpropane	51.96057	51.899	-0.00119

Table 1.9. The calculated and experimental total bond energies of alkene halides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C₂H₃Cl C₃H₅Cl	Chloroethene 2-Chloropropene	22.46700	22.505	0.00170
C3113C1	2-Cmoropropene	35.02984	35.05482	0.00071

Table 1.10. The calculated and experimental total bond energies of alcohols using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error	
Formula	Name	Total Bond	Total Bond		
		Energy (eV)	Energy (eV)		
CH₄O	Methanol	21.11038	21.131	0.00097	
C₂H <sub>6</sub> O	Ethanol -	33.40563	33,428	0.00066	
C₃H <sub>8</sub> O	1-Propanol	45.56333	45.584	0.00046	
C₃H <sub>8</sub> O	2-Propanol	45.72088	45.766	0.00098	
$C_4H_{10}O$	1-Butanol	57.72103	57.736	0.00026	
C <sub>4</sub> H <sub>10</sub> O	2-Butanol	57.87858	57.922	0.00074	
$C_4H_{10}O$	2-Methyl-1-propananol	57.79359	57.828	0.00060	
$C_4H_{10}O$	2-Methyl-2-propananol	58.15359	58.126	-0.00048	
C <sub>5</sub> H <sub>12</sub> O	1-Pentanol	69.87873	69.887	0.00048	

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
C <sub>5</sub> H <sub>12</sub> O	2-Pentanol	70.03628	70.057	0.00029
C <sub>5</sub> H <sub>12</sub> O	3-Pentanol	70.03628	70.097	0.00087
C <sub>5</sub> H <sub>12</sub> O	2-Methyl-1-butananol	69.95129	69.957	0.00008
C <sub>5</sub> H <sub>12</sub> O	3-Methyl-1-butananol	69.95129	69.950	-0.00002
C <sub>5</sub> H <sub>12</sub> O	2-Methyl-2-butananol	70.31129	70.246	-0.00092
C <sub>5</sub> H <sub>12</sub> O	3-Methyl-2-butananol	69.96081	70.083	0.00174
$C_6H_{14}O$	I-Hexanol	82.03643	82.054	0.00021
$C_6H_{14}O$	2-Hexanol	82.19398	82.236	0.00052
C <sub>7</sub> H <sub>16</sub> O	1-Heptanol	94.19413	94.214	0.00021
$C_8H_{18}O$	1-Octanol	106.35183	106.358	0.00006
$C_8H_{18}O$	2-Ethyl-1-hexananol	106.42439	106.459	0.00032
C <sub>9</sub> H <sub>20</sub> O	1-Nonanol	118.50953	118.521	0.00010
$C_{10}H_{22}O$	1-Decanol	130.66723	130.676	0.00007
$C_{12}H_{26}O$	1-Dodecanol	154.98263	154.984	0.00001
C <sub>16</sub> H <sub>34</sub> O	1-Hexadecanol	203.61343	203.603	-0.00005

Table 1.11. The calculated and experimental total bond energies of ethers using closed-form equations having integers and fundamental constants only.

	-	Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond Energy (eV) 32.902 45.183 57.500 57.355 57.499 81.817 82.088 82.033 94.438 106.122 106.410	
		Energy (eV)	Energy (eV)	
C <sub>2</sub> H <sub>6</sub> O	Dimethyl ether	32.84496		0.00174
C <sub>3</sub> H <sub>8</sub> O	Ethyl methyl ether	45.19710	45.183	-0.00030
$C_4H_{10}O$	Diethyl ether	57.54924	57.500	-0.00086
$C_4H_{10}O$	Methyl propyl ether	57.35480	57.355	0.00000
$C_4H_{10}O$	Isopropyl methyl ether	57.45569	57.499	0.00075
$C_6H_{14}O$	Dipropyl ether	81.86464	81.817	-0.00059
C <sub>6</sub> H <sub>14</sub> O	Disopropyl ether	82.06642	82.088	0.00026
C <sub>6</sub> H <sub>14</sub> O	t-Butyl ethyl ether	82.10276	82.033	-0.00085
$C_7H_{16}O$	t-Butyl isopropyl ether	94.36135	94.438	0.00081
$C_8\dot{H}_{18}O$	Dibutyl ether	106.18004	106.122	-0.00055
$C_8H_{18}O$	Di-sec-butyl ether	106.38182	106.410	0.00027
$C_8H_{18}O$	Di-t-butyl ether	106.36022	106.425	0.00061
$C_8H_{18}O$	t-Butyl isobutyl ether	106.65628	106.497	-0.00218

Table 1.12. The calculated and experimental total bond energies of 1° amines using closed-form equations having integers and fundamental constants only.

Formula		Calculated	Experimental	Relative Error
rominia	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
CH <sub>5</sub> N	Methylamine	23.88297	23.857	-0.00110
C <sub>2</sub> H <sub>7</sub> N	Ethylamine	36.04067	36.062	0.00060
C₃H <sub>9</sub> N	Propylamine	48.19837	48.243	0.00092
$C_4H_{11}N$	Butylamine	60.35607	60.415	0.00098
$C_4H_{11}N$	sec-Butylamine	60.45696	60.547	0.00148
$C_4H_{11}N$	t-Butylamine	60.78863	60.717	-0.00118
$C_4H_{11}N$	Isobutylamine	60.42863	60.486	0.00094

Table 1.13. The calculated and experimental total bond energies of 2° amines using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>7</sub> N	Dimethylamine	35.76895	35.765	-0.00012
$C_4H_{11}N$	Diethylamine	60.22930	60.211	-0.00030
C <sub>6</sub> H <sub>15</sub> N	Dipropylamine	84.54470	84.558	0.00016
C <sub>6</sub> H <sub>15</sub> N	Diisopropylamine	84.74648	84.846	0.00117
C <sub>8</sub> H <sub>19</sub> N	Dibutylamine	108.86010	108.872	0.00011
C <sub>8</sub> H <sub>19</sub> N	Diisobutylamine	109.00522	109.106	0.00092

Table 1.14. The calculated and experimental total bond energies of 3° amines using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C₃H <sub>9</sub> N	Trimethylamine	47.83338	47.761	-0.00152
$C_6H_{15}N$	Triethylamine	84.30648	84.316	0.00012
C <sub>9</sub> H <sub>23</sub> N	Tripropylamine	120.77958	120.864	0.00070

Table 1.15. The calculated and experimental total bond energies of aldehydes using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	;
		Energy (eV)	Energy (eV)	
CH <sub>2</sub> O	Formaldehyde	15.64628	15.655	0.00056
C₂H₄O	Acetaldehyde	28.18711	28.198	0.00039
C₃H <sub>6</sub> O	Propanal	40.34481	40.345	0.00000
$C_4H_8O$	Butanal	52.50251	52.491	-0.00022
C <sub>4</sub> H <sub>8</sub> O	Isobutanal	52.60340	52.604	0.00001
C <sub>5</sub> H <sub>10</sub> O	Pentanal	64.66021	64.682	0.00034
$C_7H_{14}O$	Heptanal	88.97561	88.942	-0.00038
$C_8H_{16}O$	Octanal	101.13331	101.179	0.00045
C <sub>8</sub> H <sub>16</sub> O	2-Ethylhexanal	101.20587	101.259	0.00053

Table 1.16. The calculated and experimental total bond energies of ketones using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	•
C <sub>3</sub> H <sub>6</sub> O	Acetone	40.68472	40.672	-0.00031
C <sub>4</sub> H <sub>8</sub> O	2-Butanone	52.84242	52.84	-0.00005
C <sub>5</sub> H <sub>10</sub> O	2-Pentanone	65.00012	64.997	-0:00005
C <sub>5</sub> H <sub>10</sub> O	3-Pentanone	65.00012	64.997	-0.00005
C <sub>5</sub> H <sub>10</sub> O	3-Methyl-2-butanone	65.10101	65.036	-0.00099
$C_6H_{12}O$	2-Hexanone	77.15782	77.152	-0.00008
$C_6H_{12}O$	3-Hexanone	77.15782	77.138	-0.00025
$C_6H_{12}O$	2-Methyl-3-pentanone	77.25871	77.225	-0.00043
$C_6H_{12}O$	3,3-Dimethyl-2-butanone	77.29432	77.273	-0.00028
C <sub>7</sub> H <sub>14</sub> O	3-Heptanone	89.31552	89.287	-0.00032
C7H14O	4-Heptanone	89.31552	89.299	-0.00018
$C_7H_{14}O$	2,2-Dimethyl-3-pentanone	89.45202	89.458	0.00007

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>7</sub> H <sub>14</sub> O	2,4-Dimethyl-3-pentanone	89.51730	89.434	-0.00093
C <sub>8</sub> H <sub>16</sub> O	2,2,4-Trimethyl-3-pentanone	101.71061	101.660	-0.00049
C <sub>9</sub> H <sub>18</sub> O	2-Nonanone	113.63092	113.632	0.00001
C <sub>9</sub> H <sub>18</sub> O	5-Nonanone	113.63092	113.675	0.00039
C <sub>9</sub> H <sub>18</sub> O	2,6-Dimethyl-4-heptanone	113.77604	113.807	0.00027

Table 1.17. The calculated and experimental total bond energies of carboxylic acids using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
CH <sub>2</sub> O <sub>2</sub>	Formic acid	21.01945	21.036	0.00079
$C_2H_4O_2$	Acetic acid	33.55916	33.537	-0.00066
C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	Propanoic acid	. 45.71686	45.727	0.00022
$C_4H_8O_2$	Butanoic acid	57.87456	57.883	0.00015
$C_5H_{10}O_2$	Pentanoic acid	70.03226 .	69.995	-0.00053
$C_5H_{10}O_2$	3-Methylbutanoic acid	70.10482	70.183	0.00111
$C_5H_{10}O_2$	2,2-Dimethylpropanoic acid	70.31679	69.989	-0.00468
$C_6H_{12}O_2$	Hexanoic acid	82.18996	82.149	-0.00050
$C_7H_{14}O_2$	Heptanoic acid	94.34766	94.347	0.00000
$C_8H_{16}O_2$	Octanoic acid	106.50536	106.481	-0.00022
$C_9H_{18}O_2$	Nonanoic acid	118.66306	118.666	0.00003
$C_{10}H_{20}O_2$	Decanoic acid	130.82076	130.795	-0.00020
$C_{12}H_{24}O_2$	Dodecanoic acid	155.13616	155.176	0.00026
$C_{14}H_{28}O_2$	Tetradecanoic acid	179.45156	179.605	0.00085
$C_{15}H_{30}O_2$	Pentadecanoic acid	191.60926	191.606	-0.00002
$C_{16}H_{32}O_2$	Hexadecanoic acid	203.76696	203.948	0.00089
$C_{18}H_{36}O_2$	Stearic acid	228.08236	228.298	0.00094
$C_{20}H_{40}O_2$	Eicosanoic acid	252.39776	252.514	0.00046

Table 1.18. The calculated and experimental total bond energies of carboxylic acid esters using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
	·	Energy (eV)	Energy (eV)	•
C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	Methyl formate	32.71076	32.762	0.00156
$C_3H_6O_2$	Methyl acetate	45.24849	45.288	0.00087
$C_6H_{12}O_2$	Methyl pentanoate	81.72159	81.726	0.00005
$C_7H_{14}O_2$	Methyl hexanoate	93.87929	93.891	0.00012
$C_8H_{16}O_2$	Methyl heptanoate	106.03699	106.079	0.00040
$C_9H_{18}O_2$	Methyl octanoate	118.19469	118.217	0.00018
$C_{10}H_{20}O_2$	Methyl nonanoate	130.35239	130.373	0.00016
$C_{11}H_{22}O_2$	Methyl decanoate	142.51009	142,523	0.00009
$C_{12}H_{24}O_2$	Methyl undecanoate	154.66779	154.677	0.00006
$C_{13}H_{26}O_2$	Methyl dodecanoate	166.82549	166.842	0.00010
$C_{14}H_{28}O_2$	Methyl tridecanoate	178.98319	179.000	0.00009
$C_{15}H_{30}O_2$	Methyl tetradecanoate	191.14089	191.170	0.00015
$C_{16}H_{32}O_2$	Methyl pentadecanoate	203.29859	203.356	0.00028
$C_4H_8O_2$	Propyl formate	57.76366	57.746	-0.00030
C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	Ethyl acetate	57.63888	57.548	-0.00157
C5H10O2	Isopropyl acetate	69.89747	69.889	-0.00013
$C_5H_{10}O_2$	Ethyl propanoate	69.79658	69.700	-0.00139
$C_6H_{12}O_2$	Butyl acetate	81.95428	81.873	-0.00099
$C_6H_{12}O_2$	t-Butyl acetate	82.23881	82.197	-0.00051

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	<b>Total Bond</b>	
		Energy (eV)	Energy (eV)	
$C_6H_{12}O_2$	Methyl 2,2-dimethylpropanoate	82.00612	81.935	-0.00087
$C_7H_{14}O_2$	Ethyl pentanoate	94.11198	94.033	-0.00084
$C_7H_{14}O_2$	Ethyl 3-methylbutanoate	94.18454	94.252	0.00072
$C_7H_{14}O_2$	Ethyl 2,2-dimethylpropanoate	94.39651	94.345	-0.00054
$C_8H_{16}O_2$	Isobutyl isobutanoate	106.44313	106.363	-0.00075
$C_8H_{16}O_2$	Propyl pentanoate	106.26968	106.267	-0.00003
$C_8H_{16}O_2$	Isopropyl pentanoate	106.37057	106.384	0.00013
$C_9H_{18}O_2$	Butyl pentanoate	118.42738	118.489	0.00052
$C_9H_{18}O_2$	sec-Butyl pentanoate	118.52827	118.624	0.00081
$C_9H_{18}O_2$	Isobutyl pentanoate	118.49994	118.576	0.00064

Table 1.19. The calculated and experimental total bond energies of amides using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
CH₃NO	Formamide	23.68712	23.697	0.00041
C <sub>2</sub> H <sub>5</sub> NO	Acetamide	36.15222	36.103	-0.00135
C <sub>3</sub> H <sub>7</sub> NO	Propanamide	48.30992	48.264	-0.00094
C <sub>4</sub> H <sub>9</sub> NO	Butanamide	60.46762	60.449	-0.00030
C <sub>4</sub> H <sub>9</sub> NO	2-Methylpropanamide	60.51509	60.455	-0.00099
C <sub>5</sub> H <sub>11</sub> NO	Pentanamide	72.62532	72.481	-0.00200
C <sub>5</sub> H <sub>11</sub> NO	2,2-Dimethylpropanamide	72.67890	72.718	0.00054
C <sub>6</sub> H <sub>13</sub> NO	Hexanamide	84.78302	84.780	-0.00004
C <sub>8</sub> H <sub>17</sub> NO	Octanamide	109.09842	109.071	-0.00025

Table 1.20. The calculated and experimental total bond energies of N-alkyl and N,N-dialkyl amides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>3</sub> H <sub>7</sub> NO	N,N-Dimethylformamide	47.53142	47.574	0.00090
C <sub>4</sub> H <sub>9</sub> NO .	N,N-Dimethylacetamide	59.91404	59.890	-0.00041
C <sub>6</sub> H <sub>13</sub> NO	N-Butylacetamide	84.63649	84.590	-0.00055

Table 1.21. The calculated and experimental total bond energies of urea using closed-form equations having integers and fundamental constants only.

		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	<b>Total Bond</b>	,
		Energy (eV)	Energy (eV)	
CH <sub>4</sub> N <sub>2</sub> O	Urea	31.35919	31.393	0.00108

Table 1.22. The calculated and experimental total bond energies of acid halide using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>3</sub> ClO	Acetyl chloride	28.02174	27.990	-0.00115

Table 1.23. The calculated and experimental total bond energies of acid anhydrides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_4H_6O_3$	Acetic anhydride	56.94096	56.948	0.00013
$C_6H_{10}O_3$	Propanoic anhydride	81.25636	81.401	0.00177

Table 1.24. The calculated and experimental total bond energies of nitriles using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond	Experimental Total Bond	Relative Error
1 Ollidia	Name	Energy (eV)	Energy (eV)	
C <sub>2</sub> H <sub>3</sub> N	Acetonitrile	25.72060	25.77	0.00174
C <sub>3</sub> H <sub>5</sub> N	Propanenitrile ·	37.87830	37.94	0.00171
C <sub>4</sub> H <sub>7</sub> N	Butanenitrile	50.03600	50.08	0.00082
C <sub>4</sub> H <sub>7</sub> N	2-Methylpropanenitrile	50.13689	50.18	0.00092
C <sub>5</sub> H <sub>9</sub> N	Pentanenitrile	62.19370	62.26	0.00111
C <sub>5</sub> H <sub>9</sub> N	2,2-Dimethylpropanenitrile	62.47823	62.40	-0.00132
$C_7H_{13}N$	Heptanenitrile	86.50910	86.59	0.00089
C <sub>8</sub> H <sub>15</sub> N	Octanenitrile	98.66680	98.73	0.00069
$C_{10}H_{19}N$	Decanenitrile	122.98220	123.05	0.00057
$C_{14}H_{27}N$	Tetradecanenitrile	171.61300	171.70	0.00052

Table 1.25. The calculated and experimental total bond energies of thiols using closed-form equations having integers and fundamental constants only.

		- ·		
		Calculated	Experimental	Relative Error
Formula	Name	Total Bond	Total Bond	
		Energy (eV)	Energy (eV)	
HS	Hydrogen Sulfide	3.77430	3.653	-0.03320
H <sub>2</sub> S	Dihydrogen Sulfide	7.56058	7.605	0.00582
CH₄S	Methanethiol	19.60264	19.575	-0.00141
C <sub>2</sub> H <sub>6</sub> S	Ethanethiol	31.76034	31.762	0.00005
C₃H <sub>8</sub> S	1-Propanethiol	43.91804	43.933	0.00035
C₃H <sub>8</sub> S	2-Propanethiol	44.01893	44.020	0.00003
C <sub>4</sub> H <sub>10</sub> S	1-Butanethiol	56.07574	56.089	0.00024
$C_4H_{10}S$	2-Butanethiol	56.17663	56.181	0.00009
C <sub>4</sub> H <sub>10</sub> S	2-Methyl-1-propanethiol	56.14830	56.186	0.00066
C <sub>4</sub> H <sub>10</sub> S	2-Methyl-2-propanethiol	56.36027	56.313	-0.00084
C <sub>5</sub> H <sub>12</sub> S	2-Methyl-1-butanethiol	68.30600	68.314	0.00012
C <sub>5</sub> H <sub>12</sub> S	1-Pentanethiol	68.23344	68.264	0.00044
C₅H <sub>12</sub> S	2-Methyl-2-butanethiol	68.51797	68.441	-0.00113
C₅H <sub>12</sub> S	3-Methyl-2-butanethiol	68.31552	68.381	0.00095
C₅H <sub>12</sub> S	2,2-Dimethyl-1-propanethiol	68.51797	68.461	-0.00084
C <sub>6</sub> H <sub>14</sub> S	1-Hexanethiol	80.39114	80.416	0.00031
C <sub>6</sub> H <sub>14</sub> S	2-Methyl-2-pentanethiol	80.67567	80.607	-0.00085
C <sub>6</sub> H <sub>14</sub> S	2,3-Dimethyl-2-butanethiol	80.71992	80.603	-0.00145
$C_7H_{16}S$	1-Heptanethiol	92.54884	92.570	0.00023
C <sub>10</sub> H <sub>22</sub> S	1-Decanethiol	129.02194	129.048	0.00020

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Table 1.26. The calculated and experimental total bond energies of sulfides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Tetal Part	Experimental	Relative Error
1 Ollindia	Ivaine	Total Bond	Total Bond	
CHO	701 11 17 17 1	Energy (eV)	Energy (eV)	
C₂H <sub>6</sub> S	Dimethyl sulfide	31.65668	31.672	0.00048
C₃H <sub>8</sub> S	Ethyl methyl sulfide	43.81438	43.848	0.00078
$C_4H_{10}S$	Diethyl sulfide	55.97208	56.043	0.00126
$C_4H_{10}S$	Methyi propyl sulfide	55.97208	56.029	0.00120
$C_4H_{10}S$	Isopropyl methyl sulfide	56.07297	56.115	0.00102
C <sub>5</sub> H <sub>12</sub> S	Butyl methyl sulfide	68.12978	68.185	0.00073
C <sub>5</sub> H <sub>12</sub> S	t-Butyl methyl sulfide	68.28245	68.381	0.00081
C <sub>5</sub> H <sub>12</sub> S	Ethyl propyl sulfide	68.12978	68.210	
C <sub>5</sub> H <sub>12</sub> S	Ethyl isopropyl sulfide	68.23067	68.350	0.00117
$C_6H_{14}S$	Diisopropyl sulfide	80.48926	80.542	0.00174
$C_6H_{14}S$	Butyl ethyl sulfide	80.28748	80.395	0.00065
C <sub>6</sub> H <sub>14</sub> S	Methyl pentyl sulfide	80.28748		0.00133
C <sub>8</sub> H <sub>18</sub> S .	Dibutyl sulfide		80.332	0.00056
C <sub>8</sub> H <sub>18</sub> S	Di-sec-butyl sulfide	104.60288	104.701	0.00094
C <sub>8</sub> H <sub>18</sub> S		104.80466	104.701	-0.00099
	Di-t-butyl sulfide	104.90822	104.920	0.00011
C <sub>8</sub> H <sub>18</sub> S	Diisobutyl sulfide	104.74800	104.834	0.00082
C <sub>10</sub> H <sub>22</sub> S	Ethyl propyl sulfide	128.91828	128.979	0.00047
C <sub>10</sub> H <sub>22</sub> S	Diisopentyl sulfide	129.06340	129.151	0.00047

Table 1.27. The calculated and experimental total bond energies of disulfides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
$C_2H_6S_2$	Dimethyl disulfide	34.48127	34.413	-0.00199
$C_4H_{10}S_2$	Diethyl disulfide	58.79667	58.873	0.00129
$C_6H_{14}S_2$	Dipropyl disulfide	83.11207	83.169	0.00068
$C_8H_{18}S_2$	Di-t-butyl disulfide	107.99653	107.919	-0.00072

Table 1.28. The calculated and experimental total bond energies of sulfoxides using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond	Relative Error
C <sub>2</sub> H <sub>6</sub> SO C <sub>4</sub> H <sub>10</sub> SO C <sub>6</sub> H <sub>14</sub> SO	Dimethyl sulfoxide Diethyl sulfoxide Dipropyl sulfoxide	35.52450 59.83990 84.15530	Energy (eV) 35.435 59.891 84.294	-0.00253 0.00085 0.00165

Table 1.29. The calculated and experimental total bond energies of sulfones using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond	Experimental Total Bond	Relative Error
CHEO	D:	Energy (eV)	Energy (eV)	
$C_2H_6SO_2$	Dimethyl sulfone	40.27588	40.316	0.00100

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Table 1.30. The calculated and experimental total bond energies of sulfites using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>6</sub> SO <sub>3</sub>	Dimethyl sulfite Diethyl sulfite Dibutyl sulfite	43,95058	44.042	0.00207
C <sub>4</sub> H <sub>10</sub> SO <sub>3</sub>		68,54939	68.648	0.00143
C <sub>8</sub> H <sub>18</sub> SO <sub>3</sub>		117,18019	117.191	0.00009

Table 1.31. The calculated and experimental total bond energies of sulfates using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C <sub>2</sub> H <sub>6</sub> SO <sub>4</sub>	Dimethyl sulfate	48.70617	48.734	0.00058
C <sub>4</sub> H <sub>10</sub> SO <sub>4</sub>	Diethyl sulfate	73.30077	73.346	0.00061
C <sub>6</sub> H <sub>14</sub> SO <sub>4</sub>	Dipropyl sulfate	97.61617	97.609	-0.00008

Table 1.32. The calculated and experimental total bond energies of nitro alkanes using closed-form equations having integers and fundamental constants only.

				-
Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond	Relative Error
CH <sub>3</sub> NO <sub>2</sub>	Nitromethane	25.14934	Energy (eV)	
C <sub>2</sub> H <sub>4</sub> NO <sub>2</sub>	Nitroethane		25.107	-0.00168
		37.30704	37.292	-0.00040
C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>	1-Nitropropane	49.46474	49.451	-0.00028
C <sub>3</sub> H <sub>7</sub> NO <sub>2</sub>	2-Nitropropane	49,56563	49.602	
C <sub>4</sub> H <sub>6</sub> NO <sub>2</sub>	1-Nitrobutane			0.00074
C <sub>4</sub> H <sub>9</sub> NO <sub>2</sub>	• • • • • • • • • • • • • • • • • • • •	61.62244	61.601	-0.00036
	2-Nitroisobutane	61.90697	: 61.945	0.00061
$C_5H_{11}NO_2$	1-Nitropentane	73.78014	73.759	-0.00028

Table 1.33. The calculated and experimental total bond energies of nitrite using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond	Experimental Total Bond	Relative Error
CVI		Energy (eV)	Energy (eV)	
CH <sub>3</sub> NO <sub>2</sub>	Methyl nitrite	24.92328	24.955	0.00126

Table 1.34. The calculated and experimental total bond energies of nitrate using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>3</sub> NO <sub>3</sub>	Methyl nitrate	28.18536	28.117	-0.00244
C <sub>2</sub> H <sub>5</sub> NO <sub>3</sub>	Ethyl nitrate	40.34306	40.396	0.00131
$C_3H_7NO_3$	Propyl nitrate	52.50076	52.550	0.00093
C <sub>3</sub> H <sub>7</sub> NO <sub>3</sub>	Isopropyl nitrate	52.60165	52.725	0.00233

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Table 1.35. The calculated and experimental total bond energies of conjugated alkenes using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
C₅H <sub>8</sub> C₄H <sub>6</sub>	Cyclopentene 1,3 Butadiene	54.83565	54.86117	0.00047
C <sub>5</sub> H <sub>8</sub>	1,3 Pentadiene	42.09159 54.40776	42.12705 54.42484	0.00084 0.00031
C <sub>5</sub> H <sub>8</sub> C <sub>5</sub> H <sub>6</sub>	1,4 Pentadiene 1,3 Cyclopentadiene	54.03745	54.11806	0.00149
<b>4</b> 3.20	1,5 Cyclopolitatiene	49.27432	49.30294	0.00058

Table 1.36. The calculated and experimental total bond energies of aromatics and heterocyclic aromatics using closed-form equations having integers and fundamental constants only.

Formula	Name	Calculated	Experimental	Relative Error
		Total Bond	Total Bond	
- O TY		Energy (eV)	Energy (eV)	
C <sub>6</sub> H <sub>6</sub>	Benzene	57.26008	57.26340	0.00006
C <sub>6</sub> H <sub>5</sub> Cl	Chlorobenzene	56.55263	56.581	0.00051
C <sub>6</sub> H <sub>4</sub> Cl <sub>2</sub>	m-dichlorobenzene	55.84518	55.852	0.00012
C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	1,2,3-trichlorobenzene	55.13773	55.077	-0.00111
C <sub>6</sub> H <sub>3</sub> Cl <sub>3</sub>	1,3,5-trichlorbenzene	55.29542	55.255	-0.00073
C <sub>6</sub> Cl <sub>6</sub>	Hexachlorobenzene	52.57130	52.477	-0.00179
C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	Nitrobenzene	65.18754	65.217	0.00046
C <sub>7</sub> H <sub>8</sub>	Toluene	69.48425	69.546	0.00088
$C_7H_6O_2$	Benzoic acid	73.76938	73.762	-0.00009
C7H5ClO2	2-chlorobenzoic acid	73.06193	73.082	0.00027
C <sub>7</sub> H <sub>5</sub> ClO <sub>2</sub>	3-chlorobenzoic acid	73.26820	73,261	-0.00010
C <sub>7</sub> H <sub>5</sub> ClO <sub>2</sub>	4-chlorobenzoic acid	73.26820	73.247	-0.00028
C <sub>6</sub> H <sub>7</sub> N	Aniline	64.43373	64.374	-0.00023
C <sub>7</sub> H <sub>9</sub> N	2-methylaniline	76.62345	76.643	-0.00095
C <sub>7</sub> H <sub>9</sub> N	3-methylaniline	76.62345	76.661	0.00023
C <sub>7</sub> H <sub>9</sub> N	4-methylaniline	76.62345	76.654	0.00030
$C_6H_6N_2O_2$	2-nitroaniline	72.47476	72.424	-0.00070
$C_6H_6N_2O_2$	3-nitroaniline	72.47476	72.481	-0.00009
$C_6H_6N_2O_2$	4-nitroaniline	72,47476	72.476	-0.00009
C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>	Aniline-2-carboxylic acid	80.90857	80.941	0.00041
C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>	Aniline-3-carboxylic acid	80.90857	80.813	-0.00118
C <sub>7</sub> H <sub>7</sub> NO <sub>2</sub>	Aniline-4-carboxylic acid	80.90857	80.949	0.00050
C <sub>6</sub> H <sub>6</sub> O	Phenol	61.75817	61.704	-0.00087
C <sub>6</sub> H <sub>4</sub> N <sub>2</sub> O <sub>5</sub>	2,4-dinitrophenol	77.61308	77.642	0.00037
C <sub>6</sub> H <sub>8</sub> O	Anisole	73.39006	73.355	-0.00047
$C_{10}H_{8}$	Naphthalene	90.74658	90.79143	0.00047
C <sub>4</sub> H <sub>5</sub> N	Pyrrole	44.81090	44.785	-0.00049
C <sub>4</sub> H <sub>4</sub> O	Furan	41.67782	41.692	
C <sub>4</sub> H <sub>4</sub> S	Thiophene	40.42501	40.430	0.00033
C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	Imidazole	39.76343	39.74106	0.00013
C5H5N	Pyridine	51.91802		-0.00056
C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>	Pyrimidine	46.57597	51.87927	-0.00075
C <sub>4</sub> H <sub>4</sub> N <sub>2</sub>	Pyrazine	46.57597	46.51794	-0.00125
C <sub>9</sub> H <sub>7</sub> N	Quinoline	85.40453	46.51380	0.00095
C <sub>9</sub> H <sub>7</sub> N	Isoquinoline	85.40453	85.48607	0.00178
C <sub>8</sub> H <sub>7</sub> N	Indole	78.52215	85.44358	0.00046
C <sub>5</sub> H <sub>5</sub> N <sub>5</sub>	Adenine	70.83735	78.514 70.79811	-0.00010 -0.00055

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#### Section V1

#### Software Program

The present invention relates to a system of computing and rendering the nature of at least one specie selected from a group of diatomic molecules having at least one atom that is other than hydrogen, polyatomic molecules, molecular ions, polyatomic molecular ions, or molecular radicals, or any functional group therein, comprising physical, Maxwellian solutions of charge, mass, and current density functions of said specie, said system comprising: processing means for processing physical, Maxwellian equations representing charge, mass, and current density functions of said specie; and an output device in communication with the processing means for displaying said physical, Maxwellian solutions of charge, mass, and current density functions of said specie.

In one embodiment, for example, the system comprises five components: (1) the graphical user interface (GUI); (2) the routine for parsing between an input chemical structure or name and taking the input and activating a routine to call up the parts of the molecule (functional groups), which are used for determining the energies and structure to be rendered; (3) the functional-group data base that has an organization of the theoretical solutions; (4) the rendering engine, which calculates and enables manipulations of the image, such as a three-dimensional model in response to commands, as well as responds to commands for data parameters corresponding to the image such as bond energies and charge distribution and geometrical parameters; and (5) data transfer system for inputting numerical data into or out of the computational components and storage components of the main system. The system further comprises spreadsheets with solutions of the bond parameters with output in any standard spreadsheet format. The system also comprises a data-handling program to transfer data from the spreadsheets into the main program.

The output may be, for example, at least one of graphical, simulation, text, and numerical data. The output may be the calculation of at least one of: (1) a bond distance between two atoms; (2) a bond angle between three of the atoms; (3) a bond energy between two atoms; (4) orbital intercept distances and angles; and (5) charge-density functions of atomic, hybridized, and molecular orbitals, wherein the bond distance, bond angle, and bond energy are calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration.

In other embodiments, the charge, current, energy, and geometrical parameters are output to be inputs to other programs that may be used in further applications. For example, the data of heats of formation may be input to another program to be used to predict stability (existence of compounds) equilibrium constants and to predict synthetic pathways. That is, a 5 novel composition of matter may be discovered by calculating at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of 10 atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration. The charge and current density functions may be used to predict the electric and magnetic fields of the species to determine other properties due to the interaction of the fields between species. These fields and the predictions of field interactions may be computed using Maxwell's equations. In one 15 embodiment, finite-element analysis is used to predict or calculate the interaction and resulting properties, such as the freezing point, boiling point, density, viscosity, and refractive index. Furthermore, the output data can be used to give thermodynamic, spectroscopic, and other properties, aid in drug design and other applications with or without direct visualization. Furthermore, the data can be input into other programs of the system, which calculate 20 thermodynamic and other properties, or performs a simulation, such as a chemical reaction or molecular dynamics.

The output data may be used to predict a composition of matter comprising a plurality of atoms, the improvement comprising a novel property or use discovered by calculation of at least one of a bond distance between two of the atoms, a bond angle between three of the atoms, and a bond energy between two of the atoms, orbital intercept distances and angles, charge-density functions of atomic, hybridized, and molecular orbitals, the bond distance, bond angle, and bond energy being calculated from physical solutions of the charge, mass, and current density functions of atoms and atomic ions, which solutions are derived from Maxwell's equations using a constraint that a bound electron(s) does not radiate under acceleration. The novel property, for example, may be a new pharmaceutical use, or stability at room temperature of a novel arrangement of atoms or ions.

In one embodiment, the output device of the system is a display that displays at least one of visual or graphical media. The display may be at least one of static or dynamic. At least one of vibration, rotation, and translation may be displayed. The displayed information

may be used for at least one of modeling reactivity, predicting physical properties, and aiding in drug and material design. The output device may be a monitor, video projector, printer, or one-, two- or three-dimensional rendering device. The displayed information may be used to model other molecules and provides utility to anticipate their reactivity and physical properties.

- Additionally, data may be output and used in the same and additional applications as the rendered models and representations of the calculated physical solutions. The processing means of the system may be a general-purpose computer. The general-purpose computer may comprise a central processing unit (CPU), one or more specialized processors, system memory, a mass storage device such as a magnetic disk, an optical disk, or other storage device, an input
- 10 means. The input means may comprise a serial port, USB port, microphone input, camera input, keyboard or mouse. The processing means comprises a special purpose computer or other hardware system. The system may comprise computer program products such as computer readable medium having embodied therein program code means. The computer readable media may be any available media which can be accessed by a general purpose or
- 15 special purpose computer. The computer readable media may comprise, for example, at least one of RAM, ROM, EPROM, CD ROM, DVD or other optical disk storage, magnetic disk storage or other magnetic storage devices, or any other medium that can embody the desired program code means and which can be accessed by a general purpose or special purpose computer. The program code means may comprise executable instructions and data, which
- 20 cause a general purpose computer or special purpose computer to perform a certain function of a group of functions. Commercial examples of suitable program language includes, for example, C++, C, JAVA, FORTRAN, Python and Assembly Languages, programmed with an algorithm based on the physical solutions, and the computer may be a PC, mainframe, supercomputer, or cluster of computers. Commercial examples of suitable programs include,
- 25 for example, APIs like OpenGL, DirectX, FOX GUI toolkit, and Qt. This program may be developed to run on at least one of operating systems like Windows XP, Windows 2000, Windows Vista, MAC OS, MAC OS X, Linux, Unix, Irix and other Unix-type operating systems.

Millsian software is designed to render 3-D models of molecules, molecular ions,
30 molecular radicals, functional groups thereof, and related structure and property information
and produce useful data output and application of the parameters of these species, wherein the
nature of their bound electrons and chemical bonds are solved using Dr. Randell L. Mills'
Classical Quantum Mechanics theory described in the reference: R. L. Mills, "The Grand
Unified Theory of Classical Quantum Mechanics", June 2006 Edition, Cadmus Professional

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Communications-Science Press Division, Ephrata, PA, ISBN 0963517171, Library of Congress Control Number 2005936834; posted at http://www.blacklightpower.com/bookdownload.shtml, which is incorporated by this reference in its entirety. Figure 76 provides a flow chart diagram, which is an example of a software system that can be utilized for this purpose, which example is not intended to limit the scope of the disclosed inventions. The main parts of this exemplary software system illustrated in Figure 76 will now be further explained:

Start: A user can start the program by running an executable program file. That might be done, for example, by double clicking the program icon on a Windows-based operating system, or typing the name of the executable file on the command line and pressing the 'Enter' key on a Linux or Unix operating system. The program initially starts by reading data files located in specific directories. The names of those directories and locations are fixed according to the type and format of the data files.

Data files: There are two types of data files used in the software system: functional group data files and molecule data files. Functional group data files contain information about various functional groups. Functional groups are the basic bonding elements or units that each typically comprise an atom, or at least two atoms bound together as found within a molecule (e.g. -Cl, C=C, C=O, CH3). Functional groups typically dictate or define properties and structure of the molecule. Similar functional groups in different molecules typically react in similar ways when subjected to a particular set of reaction conditions. Molecule data files contain information about molecules, molecular ions, and molecular radicals. These data files are processed according to their file formats.

File formats: Millsian software employs two kinds of file formats for storing

25 information about the structure, energies and names of molecules and functional groups: rawdata format and hierarchical format. In a raw-data file, all information is stored as is, below
the header describing the type of information. As shown in the Table below, for example, the
names of the molecule or functional group are listed below the #NAMES header. The names
and positions of the atoms are listed below the #ATOMS header, and so on.

```
#NAMES
       CH3
       Alkane CH3
       #SMILES
 5
       C-
      #ATOMS
             C
                          0
                                 0
      2
             Η
                    1.9775 -0.698 0
                                 -0.698 1.712
      3
             Η
                    -0.9888
      4
             H
                    -0.9888
                                 -0.698 -1.712
10
      #AO
                   0.171 2
      1
             1 1s
      2
             1 2sp3 0.864 -1
      #BONDS
      1
             12
                   1
                          1.649
      2
             13
                   1
                          1.649
      3
15
             14
                   1
                          1.649
      #BONDAXES
                   1
                          90
                                0
                                       0
      #DATA
      RCH bond angle: 109.44°
      CH bond length: 2.097 a
20
      HFORM: 12.492
```

Most of the functional groups files and some simple molecule files are stored in raw data format. The other file format used with the Millsian software system, the hierarchical file format, represents the information in a graph style, in which nodes are connected to other nodes through links. This format is designed to construct molecules by attaching different functional groups in a desired manner. Using this file format, the user can construct complex molecules built from solved functional groups.

For example, as shown in the Table below, the pentane data file includes a #GROUPS header below which is list all of the functional groups that form a part of the pentane molecule.

30 Under the #GROUP\_LINKS header is information about how these functional groups are connected to each other to construct pentane.

5

10

				317	<u> </u>	
#NA	MES					
Pent	ane					
	ILES					
CCC	CCC					
	OUPS					
1	C-					
2	-C-				•	
3	-C-					
4	-C-					
5	C-					
#GR	OUP_L	INKS				
1	11	21	180			
2	22	3 1	180			
3	3 2	4 1	180			
4	42	5 1	180			

Processing data files: As further shown in the flow diagram of Figure 76 for the exemplary Millsian software system, the program first processes the functional group data file and constructs the functional-group objects, which are complete 3-D representations of the functional groups and their related information supplied in the corresponding file. These objects are then ready to be visually displayed through use of a molecule viewer. Next, the program processes the molecule data file. If the molecule date file is in raw-data format, then the program makes a molecule object directly from it. If the file is in hierarchical format, then the program calculates geometric parameters from listed functional groups. The program stores all functional-group objects and molecule objects using internal data structures.

Visualization/ User Interactions: As shown in Figures 77 and 78, the molecule viewer displays the functional-group objects and molecule objects and provides basic interaction capabilities with the displayed objects, such as rotating, scaling, and moving the objects. The molecule viewer also provides other visualization options, such as viewing molecules in wire frame mode, viewing coordinate axes, and changing of the transparency and lighting. The user, for example, can also select parts of a molecule for visualization, like a nucleus, atomic orbital, molecular orbital, or bond axis. The viewer also includes a drop down information window, which provides, for example, related information about molecules, such as bond angles, component functional groups, and total heat of formation. In one embodiment, a user can create new molecules by joining functional groups. For this purpose, the user can select a

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first functional group. Next, the user can select an open bond from the functional group where the user desires to attach another group. Next, the user can select another or the same functional group, followed by selecting an open bond from the other group. The user can join the two selected functional groups at the selected open bonds by clicking on 'Join Groups'.

5 This method of joining functional groups at open bonds can be repeated to form the desired molecule.

SMILES input: The Simplified Molecular Input Line Entry Specification or SMILES is a specification for unambiguously describing the structure of chemical molecules using short ASCII strings. Through the user interface, a user can enter SMILES to construct molecules, provided the new molecule comprises functional groups that are in the database. Once a SMILES is entered, a parser reads in and breaks it down into component functional groups. The software system then attaches the component functional groups to create the new molecule object, which can then be viewed using the molecule viewer.

While the claimed invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof.

## CONTINUOUS-CHAIN ALKANES ( $C_n H_{2n+2}$ , $n = 3,4,5...\infty$ )

The continuous-chain alkanes,  $C_n H_{2n+2}$ , are the homologous series comprising terminal methyl groups at each end of the chain with n-2 methylene  $(CH_2)$  groups in between:

$$CH_3(CH_2)_{n-2}CH_3$$
 (15.109)

- 5  $C_n H_{2n+2}$  can be solved using the same principles as those used to solve ethane and ethylene wherein the 2s and 2p shells of each C hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  hybridized orbitals (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and
  - energy. Three H AOs combine with three carbon  $2sp^3$  HOs and two H AOs combine with
- 10 two carbon  $2sp^3$  HOs to form each methyl and methylene group, respectively, where each bond
  - comprises a  $H_2$ -type MO developed in the Nature of the Chemical Bond of Hydrogen-Type
  - Molecules and Molecular Ions section. The  $CH_3$  and  $CH_2$  groups bond by forming  $H_2$ -type
  - MOs between the remaining  $C2sp^3$  HOs on the carbons such that each carbon forms four bonds
  - involving its four  $C2sp^3$  HOs. For the alkyl C-C group,  $E_T(atom-atom, msp^3.AO)$  is
- 15  $-1.85836 \, eV$  where both energy contributions are given by Eq. (14.513). It is based on the energy match between the  $C2sp^3$  HOs of the chain comprising methylene groups and terminal

methyl groups.

- The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of straight-chain alkanes are given in Tables 15.4,
- 20 15.5, and 15.6, respectively. The total energy of each straight-chain alkane given in Table 15.7 was calculated as the sum over the integer multiple of each  $E_D(Grupp)$  of Table 15.6 corresponding to functional-group composition of the molecule. The bond angle parameters of straight-chain alkanes determined using Eqs. (15.79-15.108) are given in Table 15.8. In this angle table and those given in subsequent sections when  $c_2'$  is given as the ratio of two values of
- 25  $c_2$  designated to Atom 1 and Atom 2 and corresponding to  $E_{Coulombic}$  of Atom 1 and Atom 2,

respectively, then 
$$c_2' = \frac{c_2(Atom\ 2)}{c_2(Atom\ 1)}$$
.

Table 15.4. The geometrical band parameters of straight-chain alkanes and experimental values [1]	netrical bond param	eters of straight-chair	alkanes and experim	rental values [1]
Parameter	رر	$C-H(CH_s)$	C - H (CH,)	· [ . ]
	dnor5	Group	Group	
a (u <sub>0</sub> )	2.12499	1.64920	1.67122	
$c'(a_{\bullet})$	1,45744	1.04856	1.05553	
Bond Length 2c' (A)	1.54280	1.10974	1.17713	
Exp. Bond Length	1.532 (propane) 1.531	1.107 (C - H propane)	1.107 (C-H propane)	
	(butane)	(C-H butane)	(C-H butane)	
$h, c \left( \sigma_{0} \right)$	1.54616	1.27295	1.29569	
b	0.68600	0.63580	0.1150	

Table 15.5. The MO to HO intercept geometrical bond parameters of straight-chain alkanes. E. is Er (atum – atom, map² AO).

Sond E. F. F. F. F. F. Final Total

	F1014		-	٤		Final Total			-							
		(eV) Bond 1	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy C2sp'	(°)	(a) (a)	(cV) (eV) Final	$E(C2sp^3)$ (eV) Final	. <sub>θ</sub> ©	ø <sub>-</sub> ©	<b>%</b> ⊙	d, (o,)	$\begin{pmatrix} d_1 \\ a_0 \end{pmatrix}$	
(CH.)	,	9,000	,			[EA	1									
(1)	-	0147670.	0	0	•	-152.54487	17716.0	0.86359	-15.75493	-15.56407	77.49	15 61	41.40	73375		
(CH.)	٠	210000	0.0000	,									41,40	1.40364	0.18708	
,			0127270	>	•	-153,47406	0.91771	0.81549	-16.68412	-16.49325	68.47	5	36.04	, 20,20		
-C.H.C.H.	c	-0.92918	-		،							2	22.04	1,33480	0.2933	
				,	•	137.3448/	0.91771	0.86359	-15,75493	-15.56407	63.82	11618	\$0 St	07.070	20100.0	
-C,H,CH,	ບ	0.92918	-0.92918	•	٠	20121 131							20.00	67900	0.38106	
						123.47400	17.16.0	0.81549	-1668412	-16.49325	56.41	2 2	2			

Table 15.6. The energy parameters (eV) of functional groups of straight-chain alkanes.

Table 15.6. The energy parameter			T
Parameters	C – C Group	CH <sub>3</sub>	$CH_2$
	<del></del>	Group	Group
$n_{i}$	1	3	2
n <sub>2</sub>	0	2	1
n <sub>3</sub>	0	0	0
$C_{\iota}$	0.5	0.75	0.75
$C_2$	1	1	1
c <sub>l</sub>	1	1	1
<i>c</i> <sub>2</sub>	0.91771	0.91771	0.91771
<i>c</i> <sub>3</sub>	0	0	1
<i>C</i> <sub>4</sub>	2	1	1
<i>C</i> <sub>5</sub>	0	3 .	2
$C_{1o}$	0.5	0.75	0.75
$C_{2v}$	1	1	. 1
$V_{_{e}}\left( eV\right)$	-28.79214	-107.32728	-70.41425
$V_{p}(eV)$	9.33352	38.92728	25.78002
T (eV)	6.77464	32.53914	21.06675
$V_m(eV)$	-3.38732	-16.26957	-10.53337
E(AOIHO) $(eV)$	-15.56407	-15.56407	-15.56407
$\Delta E_{H_2MO}(AOIHO)$ (eV)	0	0	0
$E_{T}(AOIHO)$ (eV)	-15.56407	-15.56407	-15.56407
$E_T(H,MO)$ (eV)	-31.63537	-67.69451	-49.66493
$E_{\tau}(atom-atom,msp^3.AO)$ (eV)	-1.85836	0	0
$E_r(MO)$ (eV)	-33.49373	-67.69450	-49.66493
$\omega \left(10^{15}  rad  /  s\right)$	9.43699	24.9286	24.2751
$E_{\kappa}$ (eV)	6.21159	16.40846	15.97831
$\overline{E}_{D}$ (eV)	-0.16515	-0.25352	-0.25017
$\overline{E}_{Kvih}$ (eV)	0.12312 [2]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))
$\bar{E}_{osc}$ (eV)	-0.10359	-0.22757	-0.14502
$E_{mag}$ (eV)	0.14803	0.14803	0.14803
$E_{T}(Group) (eV)$	-33.59732	-67.92207	-49.80996
$E_{initial}(c, AO/HO) (eV)$	-14.63489	-14.63489	-14.63489
$E_{initial}(c_s AOIHO) (eV)$	0	-13.59844	-13.59844
$E_{D}(Group)$ (eV)	4.32754	12.49186	7.83016

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Table 15.7. The total bond energies of n-alkanes calculated using the functional group composition and the energies of Table 15.6 compared to the experimental values [3].

Formula	Name	ပ (	H	CH	Calculated	Experimental	Relative
			-		Total Bond Energy	Total Bond	Епог
					(eV)	Energy (eV)	
C.H.	Propane	2	2	-	41,46896	41.434	-0.00085
C.H.º	Butane	m	7	7	53.62666	53.61	-0.00036
C3H12	Pentane	4	7	"	65.78436	65.77	-0.00017
C,H11	Hexane	S	7	4	77.94206	77.93	-0.00019
C,H,k	Heptane	9	7	'n	90.09976	60.06	-0.00013
GH,	Octane	7	7	9	102.25746	102.25	-0.00006
CH <sub>28</sub>	Nonane	<b>∞</b>	7	7	114.41516	114.40	-0.00012
CleHz	Decane	6	7	<b>∞</b>	126.57286	126.57	-0.00003
C,H,	Undecane	2	~	o	138.73056	138.736	0.00004
$C_{11}H_{26}$	Dodecane	=	7	2	150.88826	150.88	-0.00008
CigH <sub>3x</sub>	Octadecane	18	7	91	223.83446	223.85	0.00008

Table 15.8. The bond angle parameters of straight-chain alkanes and experimental values [1]. In the calculation of  $\theta$ ,, the parameters from the preceding angle were used. E, is  $E_r$  and  $E_r$  is  $E_r$ 

							_
	1. Exp. θ (°)	107 (propanc)	112 (propune) 113.8 (butane)	111,0 (butane)			
יי לכווו יו	Cal. <i>θ</i> (°)	108.44	110.49	110,49	109.50	109.44	1007
יון – מנטי	(°)						
Er (and	(o) 'θ						
T. 12	(e)		15.69	15.69		70.56	3 66
וופוב שכוב וואכח.	$E_{_T}$ (eV)	0			0		
i cocuiig a	ۍ′	1.15796			96251.1		
מוו חוב ל	Մ	0.75			0.75		
מוווכובו זו	ر ک	1			-		
or, and ha	υ <u></u> .	1	:		-		
מומווסוו סו	Ç3 Atom 2.	1		_	-		
ווו וווכ כמור	C, Atom I	0.86359			0.86359		
Learning and experimental values [1]. In the calculation of $\sigma_{c}$ , the parameters from the preceding angle were used. $E_{T}$ is $E_{T}$ (then $T$ and $T$ in $T$ ).	Atom 2 Hybridization Dosignation (Table 15.3.A)	н	_		π		
ווו בעליבו ווו	Ermante Atom 1	т.			Ξ		
Contain annuice a	Atom I Hybridization Designation (Table 15.3.A)	,			7		
o sualgu	Erodounke s Atom i	15.75493 C			15.75493 C,		
allice	ZC Temir Atom	3,4252			3.4252		
מונפוג אם	2c' Band 2 ( a <sub>o</sub> )	2.1110			2,0971		
alle colle	2c' Bond i (a <sub>0</sub> )	2.11106			2.09711 2.0971 3.4252 15.73493 C.,		
Table 15:0. The bolld angle parameters of smarght-chain	Atoms of Angle	Mathrians 2.11106 2.1110 3.4252 15.75493 C.	`2''2"27	H,2,22	Methy! ZHC, H	'2'2'27 ·	H J J/

## BRANCHED ALKANES ( $C_n H_{2n+2}$ , $n = 3, 4, 5...\infty$ )

The branched-chain alkanes,  $C_n H_{2n+2}$ , comprise at least two terminal methyl groups ( $CH_3$ ) at each end of the chain, and may comprise methylene (CH<sub>2</sub>), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene 5 functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-alkane groups are solved using the same principles as those 10 used to solve the methyl and methylene functional groups wherein the 2s and 2p AOs of each C hybridize to form a single 2sp3 shell as an energy minimum, and the sharing of electrons between two C2sp3 HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy.  $E_r(atom-atom,msp^3.AO)$  of each C-C-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is  $-1.85836 \, eV$  or  $-1.44915 \, eV$  based on 15 the energy match between the  $C2sp^3$  HOs corresponding to the energy contributions equivalent to those of methylene,  $-0.92918 \, eV$  (Eq. (14.513), or methyl,  $-0.72457 \, eV$  (Eq. (14.151)), groups, respectively.

The symbols of the functional groups of branched-chain alkanes are given in Table 15.9. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. 20 (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkanes are given in Tables 15.10, 15.11, and 15.12, respectively. The total energy of each branched-chain alkane given in Table 15.13 was calculated as the sum over the integer multiple of each  $E_D$  (corresponding to functional-group composition of the molecule. The bond angle parameters of branched-chain alkanes determined using Eqs. (15.79-15.108) are given in Table 15.14.

Table 15.9. The symbols of functional groups of branched alkanes.

Functional Group	Group Symbol .
CH₃ group	$C-H(CH_3)$
CH₂ group	$C-H$ $(CH_2)$
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

	(C)	dno	.10725	1,45164	1.53635	1,532	pane)	231	(aue)	1.52750	68888
	Ĭ	ğ	2.10	1,45	1:53	<u>.</u>	fond)	- 1.5	(but	1.57	570
	(a) C-C	Group	2.10725	1.45164	1.53635	1.532	(propane)	1.53	(butano)	1.52750	202270
	( <del>g</del> )	Group	2.12499	1.45744	1.54280	1.532	(bropane)	1.531	(butane)	1.54616	002470
	(i)	Group	2,10725	1,45164	1.53635	1.532.	(propane)	1.531	(butane)	1.52750	000070
	(a) (-)-()	Circup	2.12499	1,45744	. 1.54280	1.532	(propane)	1.531	(butane)	1.54616	007070
permental varies in	(, = (, a)	Group	2.12499	1.45744	1.54280	1.532	(propane)	1.531	(butane)	1,54616	30,00
CHEC BIKANES BUG CX	H~.)	Group	1.67465	1.05661	1.11827		1,122	(isobutane)		1.29924	
1 parameters of oran	(H.) H	Group	1,67122	1.05553	1.11713	1.107	ĵ		Ŝ	1.29569	
able 15.10. The geometrical bond parameters of pranched alkanes and experimental variety	(H.) H)	Group	1.64920	1.04856	1.10974	1.107	(C - H propane)	1117	(C - H butane)	1,27295	
Table 15.10.	Parameter		0 (0,)	c. (o,)	Bond Length 2c' (A)	1000	LAP. CORD		<u> </u>	h.c (a,)	

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Table 15.11. The MO to HO intercent peometrical bond parameters of branched-clisin alkanes. R.R., R" are H or alkyl groups. Er is Er (alum - olom.asp' At).		ĺ
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Table 15.11. The MO to HO intercept geometrical bond parameters of branched-chain alkanes. R.R. R. ate H or alkyl groups. L. 15 12 (aron - origin.table - Art)	etrical band	parameters of b	ranched-cuain a	Kanes. K.K.K	are n or alky	groups. 12 15	משל מנחום	Town down							
Bond	Atom	F.	E.	E.	E,	Final Total	7.0	7.00	E (C2.40')	E(C2sp3)	,6	θ,	6	6	2,
		(eV) Bond !	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy (2xy)	(0°)	(°°)	(eV) Final	Final	©	€	©	(°)	(°)
C-H (CH,)	٤	41.92918		e	0	-152.54487	17710,0	0.146.359	-15.75493	-15.56407	77,49	102.51	41,48	1.23564	0.18708
C-H (CH,)	ن	41 929 IK	ALGZDÍK	°	c	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	33.84	1.35486	0.27933
C-H (CH)	ij	4) 92918	4192918	A1020.0-	٥	-154,40324	17719,0	0,77247	-17.61330	-17,47344	61.10	118.90	75.16	1.42988	937326
H,C,C,H,CH,	ئ	KIGZO,O-	c	c	0	-1.52.54HP	12716,0	0,46359	-15,75493	-15,56407	63,82	116.18	30.08	1.83879	0,38106
H,C,C,H,CH, -	٠,٠	41,929[H	41,9291X	5		-153,47406	17710.0	0.81549	-16.68412	-16.49325	\$6,41	123.59	36,06	1.96890	0.45117
$(R - R_1)^{-1} H_2 = (R - R_2)^{-1} H_2 H_2 - (R - R_2)^{-1} H_2 H_2 + (R - R_2)^{-1} H_2 H_3 + (R - R_2)^{-1} H_3 H_3 $	ئ	41,929 IK	41.929IX	410201F	=	-154.403A	17714,0	0,77247	-17.61330	-17,42244	48.30	131.70	21.90	1.97162	0.51388
$n - H_1C_1(R^2 - H_1C_2)C_1(R^2 - H_1C_2)CH_1 - CC_2(R)$	ن	41,92918	-0.72457	-0.72457	40,72457	-154.71860	17710,0	0.75889	-17.92866	97757.71-	43.21	131.79	21.74	1.95734	0.50570
$i\omega C_sC_s(H_1C_s-R)HCH_1-C_sC_sC_sC_sC_sC_sC_sC_sC_sC_sC_sC_sC_sC$	ن	40.92918	41,9291X	-0,92918	=	rEOr'rs1-	177160	0,77247	-17.61330	-17,42244	48.30	02.161	21.30	1,97162	0,51383
$(RHC_{*}(R'-H_{*}C_{*})C_{*}(R'-H_{*}C_{*})CH_{*}-CC_{*}(R)$		T2457	40,72457	-0.72457	-41,72457	-154.51399	17719.0	0.76765	•17.92866	-17.73779	50.04	129.96	32.66	ESHYG'I	86201.0
$IeHC_sC_s(H_1C_s - R^s)HCH_1 - (C - C_s(0))$	ť	40,72457	81626.95	#10 <u>2</u> 7.0-	9.	-154, 19863	177160	0.78155	-17.40469	-17,21783	52.78	12.22	5.6	1.97443	0.472779
$lxoC_{s}(R-H_{1}C_{s})C_{s}(R'-H_{1}C_{s})CH_{3} - (R'-C_{1}C_{1})CH_{3} - (R'-C_{1}C_{2})CH_{3} - ($	i.	72H57.0-	-0,72457	-0.72.157	12457.0-	-154,51399	17710.0	0,76765	-17.92866	-17.13779	\$0,04	129,96	32.66	1,93462	A020L.

Table 15.12. The energy parameters (eV) of functional groups of branched-chain alkanes.	ters (e.V.) of function	onal groups of br	anched-chain alkan						
Parameters	CH,	$CH_1$	H-5	~	C-C (P)	(e) D-D	C - C (d)	C-C (e)	(i) 2-2
	Group	Group	Caroup	Group	Group	Group	Group	Group	Group
, ·	3	2		1	-	-	-		-
$n_1$	2	1	0	0	0	0	0	0	6
<sup>'</sup> u	0	0	0	0	٥	0	0	C	
כ'	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.8
້ໍວ່	ı	-	-	1	-	-	-	-	
c,	1		1	-	_	_	-	-	-
5	0.91771	0.91771	0.91771	0.91771	0.91771	0.91771	177160	0.91771	0.91771
້ຳ	0	-	1	0	0	0	-	-	0
.5	-	-		2	2	2	2	2	2
6,	3	2	-	0	0	0	0	0	0
C <sub>E</sub>	0.75	0.75	0.75	0.5	0.5	5.0	0.5	0.5	0.5
٠٠٠	-	_	-	1	1	1	ı	-	-
V, (eV)	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (&V)	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
1 (eV)	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
(eV)	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(sama) (eV)	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$\Delta E_{H_3 sr}(snim)$ (eV)	0	0	0	0	0	0	0	0	0
$E_{\tau}(.mim)$ (cV)	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_r(n_2m)$ (eV)	-67.69451	-49.66493	-31.63533	-31,63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_{\tau}(atom - atom, msp^3.AO)$ (eV)	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
E_{1,m} (eV)	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω (10's rad/s)	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9,43699	9.55643	9.55643
$E_{\kappa}$ (eV)	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$E_n$ (eV)	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$E_{\text{kink}}\left(eV ight)$	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312	0.17978	0.09944 [5]	0.12312	0.12312	0.12312
E (eV)	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Emer (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_r(\iota_{tunr})$ (eV)	-67.92207	-49.80996	-31.70737	-33.59732	-33,49373	-33.24376	-33.59732	-33.18712	-33.18712
Emile, will) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Einhind (c. : 171117) (eV)	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
En (itum) (CV)	12.49186	7.83016	3,32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Formula	Мале	CH,	÷.	$CH_1$ $CH$ $C-C(a)$ $C-C(b)$ $C-C(c)$ $C-C(d)$ $C-C(c)$	C - C (a)	(e) と-こ	C-C (c)	(P) 2-2	C-C (e)	C-C (f)		Experimental	Relative Error
C.H.	Irohitana	,									Formy (eV)	Total Bond	
CH.	[socet/ana	n m	- c		۰.	m ·	0	0	0	0	53 69922	309 63	50000
Ę.	Necosniana		- <	- «	(	η.	0	0	0	0	65.85692	65.843	10000
. H	2-Methylpentane		> 1	۰ د	۰,	0	4	0	•		9229859	(4 00)	170000
C.H.	2-Metholinentine		7 (		7	•	0	Đ	0.		78 0 1467	76 007	0.000
	a de la companya de l	`	7	_	7	•	0	_	•		10.00	100.01	2.000.0
בא ה	2.2-Dimethylburane	4	_	0	_		•	> <	> 0		78.01462	616,77	-0.00046
C,H.	2,3-Dimethylbutme	4	c	,	٠ .	• •		> -	>	0	78.02106	78,124	0.00132
C,H <sub>s</sub>	2-Methylhexane	**	-				۰ د	_	0	0	77.99581	78.043	0.00061
C,H,	3-Methylhexme	. ~	3 6		<b>.</b>	٠,	0	•	0	٥	90.17232	90.160	-0.00014
CH.	3-Ethylpentime	۰ ۳	٠.		٠.	<b>,</b>	0	0		0	90.17232	7,17	13000
CHIS	2.2-Dirrethyloentene	. 4	۰.	- «	n (	m	0	•	۰	C	90.17232	20 00	-0.000
CH	2.2.3-Trimethylbutane		۷ د	> -	7	0	*		0	c	90.17876	90 276	70000
C'H.	2.4-Dimethylpentane		> -	- •	<b>.</b>	r•)	~	0	0		90.22301	57.00	20000
T.	3 3-Dirrettivinentine		- 1	~ •	0	•	0	0	0		90 24488	2000	0.0004
±	2 Martin Character	<b>.</b>	7	0	2	0	7	0			20.17076	20,23	-0.00013
	S. S	~	4	_	7	•	0	-		• •	0/0/1/0/	177'DC	0.00054
	3-Methylheptane	m	4	-	4	P*1			> <	<b>-</b>	102.33002	102,322	-0.00008
E E	4-Methylheptane	m	4	_	4		> <	> 0	> 1	>	102.33002	102.293	-0.00036
H.	3-Ethylhexane		4	_				j (	ь	0	102,33002	102,286	-0.00043
Ç,H	2,2-Dimethylliexane	4		- c	۰, ۳	• •	٠.	<b>.</b>	0	0	102,30169	102.274	-0.00027
C,H,	2,3-Dimethylhexane	4	, ~	۰,		= =	₹ (	۰.	0	0	102.33646	102.417	0.00079
C,H,H	2,4-Dimethylhexane	٧	. ~		٠ -	,	۰ د	_	0	0	102,31121	102.306	-0.00005
C,H,	2.5-Dimethylhexme	. 4	۰, ۲	۰, ۲		۰,	۰.	0	0	0	102,40258	102.362	-0 00040
C,H,	3.3-Dinethyllexane	- 4	4 ~	٠.	- •	c	0	0	0	0	102,40258	102 396	90000
H.J.	3,4-Dinethyllexane	. 4	, c	> ~	7 (	۰.	₹.	•	0	0	102,33646	102.369	0.00032
CHH	3-Ethyl-2-methylpentane	- 4	۰ ۲	4 (	7 (	•	<b>o</b> (	<b>-</b>	0	0	102,31121	102.296	-0 00015
C,H,	3-Ethyl-3-methylpentane	. 4	۰, د	۷ د	7 6	σ (	ο.	_	0	0	102,31121	102.277	-0 00033
C,H,	2.2.3-Trimethylpentane		,	- ڊ	<b>n</b> -	91	4	0	0	0	102,33646	102.317	610000-0-
Ç,H,	2.2.4-Trimethylpentane				- «	7	<b>.</b>	0	0	_	102,38071	102.370	-0.00010
Car	2,3,3-Trimethylpentane				> -	۰,	•	0	0	0	102,40902	102.412	0.00003
C,H,II	2,3,4-Trimethylpentane	۰ ۷	۔ د	- ,-	- c	~ •	m (	0	0	-	102,38071	102,332	-0.00048
CH.	2,2,3,3-Tetramethylbutans	ۍ د		,	> <	^ <	۰ د	7	•	0	102,29240	102.342	0.00049
C,H;s	2,3,5-Trimethylhexane	· <b>v</b> 1	,	۰,	> <	- r	•	0	_	0	102.41632	102.433	0.00016
C,H,,	3,3-Diethylpentane	4	- ~4	•	•	٠,	<b>-</b>	-	0	0	114,54147	114.551	0.00008
C.H.	2.2.3.3-Tetramethyloentans					<b>o</b>	đ	•	0	0	114.49416	114 455	AF0000-
CH.	2,2,3,4-Tetramethyloentans	<b>&gt;</b> 'c		? r	- «	۰,	9	0	-	0	114.57402	114,494	-0 00070
CoH;	2.2 4 4-Tetramethylnentane		• -	4 (	> 1	~	m	_	0	_	114 51960	114.402	70000
CoH.	2.3.3.4-Tetramethylmentans	2 4	- «	۰ د	۰.	0	œ	٥	0	•	114.57316	114.541	-0.00024
H.H.	2-Methylponene	, ,	۰ د	7	0	•	7	0	0	7	79285 711	114.484	70000
G.F.	2-Menymonane 2-Menhymonane	٠.	9		9	m	o	0	0	10	126 64 542	136.480	-0.00086
	- Inchigane		9	_	•	•	0	0			200000	120.000	770000
							,	,					

Table 15.14.	The bond	angle pa	rameters	of branched-	Table 15.14. The bond angle parameters of branched-chain alkanes and	d experiment	and experimental values [1]. In the calculation of $\theta_{\star}$ , the parameters from the preceding angle were used. $E_{\tau}$ is $E_{\tau}(atom-atom, msp^{\star}.AO)$	re calculati	on of $\theta$ , th	e paramete	rs from the	preceding	g angle wer	e used. $E_T$ is $E_i$	, (atom –	-atom,m	15p'. AO).		
Atoms of Anglo	2 <i>c*</i> Bernd 1 ( <i>a<sub>q</sub></i> )	2c' Bund 1 (o <sub>n</sub> )	2c' Terminal Atoms (a <sub>0</sub> )	Erminentie Alam I	Atom I Hybridization Designation (Table 15.3.A)	Erminarkie Atom 2	Atom ? Hybridization Designation (Table 15.3.4)	C <sub>2</sub> Atom I	C, Alom 2	ט'	ڻ ٽ	5	٧	<i>E</i> <sub>τ</sub> (eV)	ø, ©	<u>6</u> .©	6.0	j o €	Exp. 0
Mathy lane LHC, H	2.11106	211106	3.4252	-15.75493	7	×	н	0.86359	-	-	-	57.0	1.15796	0		-	ž	108.44	107 (propane)
۲C,C,C,														·	69.51		=	) (49	112 (propane) 113.8 (butane) 110.8 (fsobutane)
ZC,С,Н												-			15.69		=	110.49	111.0 (butane) 111.4 isobutane)
Methyl ZHC, H	2.09711	2.09711	3.4252	-15.75493	7	` н	ж	0.86359	-	-	-	0.75	1.15796	0			=	109.50	
ZC, C, C,															70.56		٦	109.44	
ZC,C,H															70.56	-	<u>-</u>	109.44	
<i>حداد د.</i> نه در	2.91547	2.91547	4.7958	-16.68412 C <sub>k</sub>	25	-16.68412 C.	. 23	0.81549	0.81549	-	-	-	0.81549	-1,85836			=	110.67	110.8 (isobutane)
4, C, C, H	2.91547	2.11323	4.1633	-15,55033 C,	\$	-14.82575 C <sub>A</sub>		0.87495	17716.0	0.75		0.75	1.04887	6			=	110.76	
"2" C" H	2.91547	2.09711	4.1633	-15.55033 C,	۶	-14.82575 C <sub>3</sub>	-	0.87495	17716.0	0.75	-	0.75	1.04887	o			=	111.27	111.4 (isobutane)
2C,C,C,	2.90327	2.90327	4.7958	-15.55033 C,	3	-14.82575 C.		0.87495	17716.0	0.75	-	0.75	1.04887	-1,85836			=	11127	111.4 (isobutane)
7C'C C'												-			72.50	-	=	107.50	

## ALKENES $(C_n H_{2n}, n = 3, 4, 5...\infty)$

The straight and branched-chain alkenes,  $C_n H_{2n}$ , comprise at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. The double bond may be bound to one, two, three, or four carbon single bonds that substitute for the hydrogen atoms of ethylene. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, three distinct functional groups can be identified: C vinyl single bond to -C(C) = C, C vinyl single bond to -C(H) = C, and C vinyl single bond to  $-C(C) = CH_2$ . In addition,  $CH_2$  of the  $-C = CH_2$  moiety is an alkene functional group.

The alkyl portion of the alkene may comprise at least two terminal methyl groups (CH<sub>3</sub>) at each end of the chain, and may comprise methylene (CH<sub>2</sub>), and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds 15 can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkenes are equivalent to those in branched-chain alkanes. The solution of the functional groups comprises the hybridization of 20 the 2s and 2p AOs of each C to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two C2sp3 HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy.  $E_r(atom-atom, msp^3.AO)$  of the C=Cbond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of ethylene,  $-2.26759 \, eV$ , given by Eq. (14.247).  $E_r(atom-atom, msp^3.AO)$  of each 25 C - C-bond MO in Eq. (15.52) is  $-1.85836 \, eV$  or  $-1.44915 \, eV$  based on the energy match between the C2sp3 HOs corresponding to the energy contributions equivalent to those of methylene,  $-0.92918 \, eV$  (Eq. (14.513), or methyl,  $-0.72457 \, eV$  (Eq. (14.151)), groups, respectively.

The symbols of the functional groups of alkenes are given in Table 15.15. The 30 geometrical (Eqs. (15.1-15.5) and (15.41)), intercept (Eqs. (15.71-15.78)), and energy (Eqs.

(15.6-15.11) and (15.17-15.56)) parameters of alkenes are given in Tables 15.16, 15.17, and 15.18, respectively. The total energy of each alkene given in Table 15.19 was calculated as the sum over the integer multiple of each  $E_D(G_{PRIMP})$  of Table 15.18 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage 5, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(G_{PRIMP})$  (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkenes determined using Eqs. (15.79-15.108) are given in Table 15.20.

alkenes, Oroup Symbol	(i) (j-t) (j-t)	$C - C \cdot (iii)$ $C - H \cdot (CH_1) (i)$	C-H (CH <sub>3</sub> )	$C = H \left( CH_1 \right) $ (ii)	(a) (b) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c	(S) (C) (C) (C) (C) (C) (C) (C) (C) (C) (C	(a) (b) (c) (c)	Ø.3-0
Table 15.15. The symbols of functional groups of alkenes. Functional Group	CC double bond C vinyl single band to -C(C)=C	C vinyl single band to -C(C))-CH,	CH, group	CH, alkyl group	CC bond (n-C)	CC bond (iso-C)	CC (iso to Iso-C)	CC (t to iso-C)

			~						_	7	$\neg$	
C-C (f) Group	2.10725	1 45164		1 53635			(propane)	(buttene)	03000	1.527.50	0.68888	
C-C (e) Group	2,10725	271371	2017	36363	CCOCC.		1,532 (propane)	(butane)		05/75.1	0.68888	
Group Group	212499	77637	1.45/44		1.34480		1,532 (propæne)	1.531 (butane)		1.54616	0.68600	
Group	2 (0725		1.43164		1,53635		L.532 (propane)	1.53) (hutane)		1.52750	0.68888	
C-C (b) Group	2 12400	4.16427	1.45744		1.54280		1,532 (propane)	1,531 (butane)		1.54616	0.68600	
C-C (a) Oroup	00700	4.17439	1,45744		1.54280		1.532	1.531 (hultane)	,	1.54616	0.68600	20000
C-H Group		1.67465	1 05661		1.11827		1133	(isobutane)		1 29924	0 63006	0,0000
$C-H\left(CH_{k}\right)$ (6)	Group	1.67122	1 05551	COCCO!	1.11713		(C-H	1.117	butane)	1 30560	100.62	0.03139
C-H (CH <sub>3</sub> ) C		1.64920	73070	0.000	1,10974		1, 107 (C - H	propare)	hurane)	2000	6.777'1	0.63580
( - H (CH,)	_ 1	1.64010		1.04.566	1 10668		1.10	(2-methylpropene) 1,108 (avg.)	(L.Jbutadiene)		1.26354	0.63756
C-((ii) Group		2.04740		1.43087	TEALS	CE IC.		1.508 (2-methy/propene)			1.46439	0.69887
('-('ii) Group		2.04740		1,43087	EGFTG	1.51437		1.508 (3-butene)			1,464,79	0.69887
parameters of alke		7 04740		1.43087		1.51437					1.464.39	0.69887
Table (5. 16. The geometrical band parameters of alkenes and experimental Parameter $C = C$ (1('(i)) ('-4'(ii)) ( Group Group Group Group		00000	077/6"	1,26661		1,34052	1.342	1,346 (2.bumb)	1.349	(1.3-bandiene)	0.75055	01038
Table 15.16. The Parameter			0 (0°)	c' (a,)	Bond Length	20' (1)	T	Length			10 (0)	

Table 15.17. The MO to HO intercept geometrical bond parameters of alkenes. It is an alkyl group and R.R.R. are H or alkyl groups.	netrical bon.	d parameters of	alkenes. 14 is a.	n alkyl group an	d R.R., R" are I	H or alkyl grou		$E_r$ is $E_r(atom - atom, msp^3, AO)$	15th, 40).						
Болд .	Atom	(eV) Bond 1	(eV) Bond 2	(eV) Bond 3	E, (eV) Bond 4	Final Total Energy C.2sp <sup>3</sup>	(a,)	(a) (a)	E <sub>c</sub> (C24°) (eV) Final	$E(C2m^3)$ (eV) Final	.6 (•)	, (o)	° (o)	(a,)	
$C_{r}(H)C_{s} = C_{s}(H)C_{s}$		-1.13320	-0.92918	٥	c	-153.67867	177100	0,80561	-16.88873	-16.69786	127.61	52.39	58.24	0.77492	1
$C_{\bullet}(H)C_{\bullet} = C_{\bullet}H_{\bullet}$	Ċ.	-1.13320	c	с	0	-152.74949	17716.0	. C5E58'0	-15.95955	-15.768GR	129.84	50.16	60,70	0.72040	1
$\vec{C_i}(C_i)C_j = C_iH_iC_j$	ن.	-1.13380	-0.72457	-0.72457	0	-154,19463	17716.0	0.78155	-17.40869	-17.21783	126.39	53.61	56.95	0.80289	ă
$R(C, H_1 - C_s(C) = C)$ (C - C (i))	ć.,	-1.13340 ·	-0.72457	-0.72457	υ	-154,19163	17716.0	0.78155	-17.40869	-17.21783	60.88	119.12	67.72	1.81127	0.3
$RC_{a}H_{3} - C_{a}(G) = C$ $(C - C_{a}(G))$ $RC_{a}H_{3} - C_{a}(G) = CH_{4}$ $\{(C - C_{a}(G))\}$	ڻ	41.72457	0.92918	, ·s	c	-153.26945	17716.0	0,425/2	16,47951	-16.28864	0r' <i>L</i> 9	112.60	31.36	1,74821	8
$R_iC_iH_1 - C_i(H) = C$ $(C_i - C_i(ij))$	ų.	-1.133×0	RIGZGO	c	U	-153,678.66	177100	0,80561	-16.83X73	-16 69786	64.57	115.43	29.79	1.77684	8
$R(',H_1-(',H)=C)$	ť.	410 <u>2</u> 0,0-	H1020:0-	٥.	u	-133,47405	17710.0	QRIS49	16.68411	-16.49325	65.99	114,01	30.58	1.76270	2.0
$C-H\left(CH_{1}\right)\left(0\right)$	ن	-1.133XD	6	υ	С	-152.74949	17716.0	0.85252	-15.95935	-15.76868	77.15	102.85	41,13	1.23531	ē
C-H (CH,)	ij	*1626'0-	o	a	5	-152,54487	17716,0	0,86359	-15.75-403	-15.56407	77.49	102.51	41,48	1.23564	ě
$C-H(CH_1)$ (ii)		-0,929{H	M1020,0-	b	ū	-133 47406	17710,0	0.81549 .	-16 68412	-16.49325	68.47	11.53	35.84	1.35486	0.25
C-H (CH)	Ü	40,92918	40.9Z918	-0.92918	С	154 40324	17710.0	0.17247	-17.61330	-17.42244	61.10	118.20	31.37	1.42988	0.37
$H_1C_s(\zeta,H_1CH_1 - (C-C_s(a)))$	Ü,	-0.92918	0	a	0	-132.54487	11710.0	0,86359	-15.75493	-15.56407	53,62	116.18	30.08	1.13879	0.31
$H_1C_1C_1H_1CH_1-$ $(C_1C_1C_1)$	C.	4.92918	K1026 0+	c	e	153,47406	17716,0	0.81549	-16.64412	-16,49325	16.62	123.59	24.06	1.90830	6
$R - H_3C_sC_s(H_3C_s - R)HCH_1 - (C - C_s(b))$	٠,٠	816260-	a.ozbik	40.92918	c	-154.4034	0.91771	0.77247	-17.61330	-17,42344	OC'RP	R.IE	21,90	1.97163	15.0
$R - H_1C_2(R - H_1C_2)C_2(R - H_2C_2)C_2H_2 - (C - C'(2))$	ď	-(1.929fk	41,72457	-4,72457	-0,72457	-134.71860	0,91771	0.75889 .	-17.92kGG	-47.7779	18.21	67.161	21.74	1.95734	0.50
$\{C_{i},C_{i},\{H_{i}C_{i}-R_{i}\}HCH_{i}-\{C_{i}-C_{i}\}\}$	ڻ	-0.9291K	*16261F	-0.9291K	0	-154,4734	17719,0	0.77247	-17.61330	17,4224	48,30	07.161	21.90	1.97162	2
$ter(C_s(R^*-H_1C_s)C_s(R^*-H_1C_s)CH_1 - (C_1-C_1(e))$	ť	-0.72457 .	-0.72457	-0.72457	-0.72457	-154,51399	0,91771	0.75765	17.92866	67.67.71-	50,04	32.621	22.06	1.94462	0,40
len(',C',(H,C,-R')HCH,-(C'-C',0))	ť	41,72457	¥16261+	ж1626 บ-	ę	-154,19863	17716,0	0.78155	-17,40869	-17,21783	32.78	17.73	24.04	1.92443	0,47
$  i_{M}(C_{i}(R^{-} + H_{i}C_{j})C_{i}(R^{-} + H_{i}C_{j})C_{i}H_{i} - H_{i}C_{j})C_{i}H_{i} - H_{i}C_{i}H_{i}C_{j}H_{i} - H_{i}C_{i}H_{i}C_{j}H_{i} - H_{i}C_{i}H_{i}C_{j}H_{i} - H_{i}C_{i}H_{i}C_{j}H_{i} - H_{i}C_{i}H_{i}C_{j}H_{i} - H_{i}C_{i}H_{i}H_{i}C_{i}H_{i}C_{i}H_{i}C_{i}H_{i}C_{i}H_{i}C_{i}H_{i}C_{i}H_{i}C_{i}H_{i}C_{i}H_{i}C_{i}H_{i}C_{i}H_{i}C_{i}H_{i}C_{i}H_{i}H_{i}C_{i}H_{i}C_{i}H_{i}C_{i}H_{i}H_{i}C_{i}H_{i}H_{i}H_{i}C_{i}H_{i}H_{i}H_{i}H_{i}H_{i}H_{i}H_{i}H$	ئ	-0.72457	tsrtt.	-11,72457	-0,72457	018181819	17719	0.76765	-17,92866	64767.11.	20.05	12098	30 £	1 03.163	;

Table 15.17. The MO to HO intercept geometrical bond parameters of alkenes. It is an alkey troum and R. R. R. are H or alkey mounts. E. is. E. farom—aron men. M.

Table 15.18. The energy parameters (eV) of functional groups of alkenes	rs (eV) of func	tional groups	of alkenes.											0
Parameters	O all of the contract of the	C-C (i)	C-C (ii)	C-C (iii)	CH <sub>2</sub> (i)	, C.	CH <sub>2</sub> (ii)	C - H Group	C-C(a) Group	(e) Group	(9) U-U	C-C (4)	Group	Group
	2	-	-	-	2	3	2	-	-	-	-	1	-	-
		0		6	-	2	-	0		0	0	0	0	0
",	,	, ,	,   c			0	0	0	0	0	0	0	0	0
4,	0.0	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
5	122100	3 -	-	-	-	-	-	-	-	-	-	-	-	-
		-	-	-	-	-	-	-	-	-	-	-	-	-
1,	122100	0 91771	0.91771	12210	12716.0	. 0.91771	17716.0	0.91771	0.91771	17716.0	17716.0	17716.0	0.91771	0.91771
5	0		0	-	-	0	-	-	0	0	0	-	-	0
2	4	2	2	2	-	;	-	-	2	2	2	2	2	2
	0	0	0	0	2		2	-	0	0	0	0	0	0
- 0	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
•	17716.0	-	-	-	_	-	-	_	_	1	-		1	
V (eV)	-102.08992	-30.19634	-30.19634	-30.19634	-72.03287	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29,10112
V, (eV)	21.48386	9.50874	9.50874	9.50874	26.02344	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	34.67062	7.37432	7.37432	7.37432	21.95990	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_ (8V)	-17,33531	-3.68716	-3.68716	-3.68716	-10.97995	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3,38732	-3.45250	-3.45250
E(vino) (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-1535946	-15.35946
DE se (noun) (eV)	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Er (.o.mo) (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
E, (11,210) (eV)	-63.27075	-31,63534	-31,63534	-31.63534	-49.66437	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	.31.63535	-31.63537	-31.63535	-31,63535
$E_{r}(atom - atom, msp^{3}, AO)$ (eV)	-2,26759	-1.44915	-1.85836	-1.44915	0	0 .	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
E, (141) (eV)	-65.53833	-33.08452	-33.49373	-33.08452	-49.66493	-67.69450	49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω (101° rad/s)	43.0680	15826	16.4962	9.97851	25.2077	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
Er (eV)	28.34813	6.56803	10.85807	6.56803	16.59214	16.40846	15.97831	15.91299	6.21159	6:21129	10.19220	6.21159	6.29021	6.29021
Ē, (eV)	-0.34517	-0.16774	-0.21834	PLL91.0-	-0.25493	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Ex., (eV)	0.17897	0.15895	0.09931	[8]	0.35532 Eq. (13.458)	0.35532 · Eq. (13.458)	0.35532 Eq. (13.458)	0.35532 Eq. (13.458)	0.12312 [2]	0.17978 [4]	0.09944 (5]	0.12312 [2]	0.12312 (2]	0.12312 [2]
Ē_ (eV)	-0.25568	-0.08827	-0.16869	-0.11809	-0.07727	-0.Z27S7	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E (eV)	0.14803	0.14803	0,14803	0.14803	0.14803	- 0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Er (inay) (eV)	-66.04969	-33.17279	-33.66242	-33.20260	-49.81948	-67.92207	-49.80996	-31,70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
E (c*1118) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Einhas (e. with) (eV)	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	0	0	٥	٥	0	0
En (comp) (aV)	7,51014	3.75498	4.39264	3.78480	7.83968	12.49186	7.83016	3,32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

values base	Values based on composition as French		1	., .,	ر	10 17.7	7.,	(2) 12)	3	را	0	(1)	ن		9	l:	Calculated	Experimental	Kelanve
	Nation Nation	ن ا ا	ĭ∈	Œ	Œ	e 5	Ŝ	(ii) :	ş	}€	}€	(@	,'€	<u>;</u> e	3	ţ	Total Bond	Total Bond	Ептог
7.	Beengle		-	-	6	-	-	0	-	6	0	0	0	0	0	0	35,56053	35.63207	0.00201
<b>.</b>	- Coperation	> -		- c						, -							67.71803	47 78477	0.00140
Ē:	-Burghe		ه د	> 1	•	- «	٠,	• <	- r	٠ ,	• =	• •		· c			91116	30500 47	-0.00057
Ť	trans-2-Butene		> 0	۹,			7 (	> 0	4 0	> 0							A1 500 TA	47 96096	0.00171
Į	Isobutene	_	0	<b>.</b>	7		7 .	> (	۰ د	۰ د	> 0	> <			•		10000	200000	1000
į	4-Pentene	_	0	-	<b>-</b>			7	-	_	<b>.</b>	<b>.</b>	<b>.</b>	٠ د	٠ د	<b>&gt;</b> (	27.6/2/2	39.93094	0.0012
C <sub>3</sub> H <sub>t</sub>	trans-2-Pentene	-	٥	7	0	0	7		7	-	0 (	0 (	<b>.</b>	۰ د	•	0 (	98880.09	00.06287	CEOO.0-
H.	2-Methyl-1-butene	-	0	0	7	-	7	-	0	-	0	0	0	0	0	0	60.06084	00.09/0/	0.0000
Ŧ.	2-Methyl-2-butene	_	-	_	0		יי	0	-	•	c	0		0	•	0	6021433	60.15444	-0.00083
Ë	3-Methyl-1-butene		٥	-	0	-	m	0	7	c	7	0	0	0	0	0	59.97662	60.01727	0.00068
£	1-Hexene	-	0	_	٥	-	-	m	-	m	0	0	0	0	0	0	72.03343	72,12954	0.00)33
ž	trans-2-Hexene	_	0	7	0	0	7	7	7	7	0	0		0	٥	0	72,24656	72,23733	-0.00013
÷	mans-3-Hexene	_	0	7	0	0	7	7	7	7	•	0	0	0	0	0	72.24656	72.24251	-0.00006
	2-Melhol. 1-nembers	-			7	-	7	2	0	7	0	0	0.	0	0	0	72,21854	72,29433	0.00105
ë :	The day of the second		, r	• -	. <	٠		. –	. –	. –		c	c	c	c	0	72.377.03	72.37206	0.00000
<u>.</u>	t-Meily-2-paints		۱ د			· -	, ,	. –	٠,					c	-	0	72.13432	72 19173	0.00080
Ē:	J-Pachyl-1-ponene		, (				1 0		• ^		, 1-			. c			72 10599	85012 62	0.00145
2	4-Meinyi-1-pentene		•	-	,	- «	4	-		•	•	•	•	,	•	,			
CaHu	3-Methyl-trans-2-	-	2		0	>	m	-	_		0	0	0	0	0	0	72,372,03	72,33268	-0.00054
	pentene					•													
C,H,	4-Methyl-trans-2-	-	0	7	0	>	m	c	m		7	0	0	0	0	0	72.34745	72.31610	-0.00043
	peniene	•	•	•	,	-	,	,	•	•		•	c	<	c	c	77 21854	25000	95,000.0
Ę,	2-Ethyl-1-butche		> 0	> 0	ч г		٠,	4 6	• •	+ <		•	•	•	o c		77 21043	23 543	0.0000
Ę.	2,3-Dimethy-I-bulene		<b>-</b>	۰ د	N (		٠,	۰ د		۰ د	4 6	> r	> 0	> <	> 0	٠,	2017	C#C2C.2/	0,000
:: T	3,3-Dimethy FI -butene	_	9		9		۹.	۰ ،	- •	۰ د	> <	1 (			> 0	7 (	27777	20,505.00	0.00020
Ŧ.	2,3-Dimethyl-2-butene	<b>-</b> .	4	۰ ۰	۰.	۰.	<del>.</del>	۰,	٥.	۰ د	<b>&gt;</b> 0	- 0	•	> <	<b>-</b> 6		04 10113	05 40527	00000
Ŧ	1-Heptene	_	0		<b>3</b> (		- 1	<b>.</b>	- •	<b>.</b>	<b>.</b>	- 0		> <		•	03676 70	*0070° 70	60000
7	5-Methyl-1-hexene	_	0		۰ د	- (	٧.	7 (	۷.	- 1	<b>n</b> (			٥ ،		•	COCO7: NO	- 11 CX X9	00000
Ŧ	trans-3-Methyl-3-hexene	-	7		9 1	۰ و	<b>^</b> 1	7.		7 (	۰ د	5 9	- <	> <	<b>-</b>	•	044480	21124,00	20000
₹.	2,4-Dimethyl-1-pentens		c	۰.	~		n (			> 0	2 6	2 •	<b>.</b>	> 0	> <	> <	04.44.000	24 47087	97,000,0
T'H'	4,4-Dimethyl-1-pentene		0		۰ د	- •	η.	- (		<b>5</b> 6	<b>&gt;</b> f	+ 0	> 0	۰ د	> <	> 0	21012.40	0014.40	0.000
ž	2,4-Dirnethyl-2-pentene	-	7	_	٥	<b>-</b>	4	>	7	>	7	5	>	>	>	>	700000*9		70,00,0-
C;H,	rrans-4,4-Dimethyd-2-	-	0	7	0	9	4		7	0	0	m	ó	0	۰	Ģ	84.54076	84.54549	0.00006
	7.Filwl-3-nethvl-1-					_					•	•	•		•			01077	1,000
ŽH.	butene	-		9	7		•	-	-	-	7	,	>	>	>	>	51//17	01641.10	-C. 00.33
á	2,3,3-Trimellyd-I-	-	•	<	,	<b>-</b> ,	4	c	c	c	c	£**.	0	0	0	?	84.51274	84.51129	-0.00002
2	buteno	•	•	,					1							. ,			
E.H.	1-Octens	_	0	0	_	<b>-</b> .	_	<b>~</b>	_	S	0	0	o;	0	0	•	96,34883	96.41421	0.00068
C.H.	trans-2,2-Dimethyl-3-	_	0	2	0	0	4	-	7	-	0	٣	0	0	0	ņ	96.69846	96.68782	-0.0001
i	hexens					-													
C,H,	3-Eulyi-4-methyl-1-	-		0	7	-	٣	7	_	7	2	0	0	٥	۰	0	96.63483	96.61113	-0,00025
	peniene 2 4 4-Trimmhul-1					-									•	•			
CAHIL	ocalene	_	0	•	~		4	-	0		Ь	4	5	5	>	>	26.0129	70.71084	0.0010
3	2,4,4-Trimathyl-2-	•	,	-	c	0		c	-	•	c	•	c	c		17	06.67590	96.65880	-0.00018
• c	penteno	,	7	-	>		•	•	•	•	•	,	,	, ,	•	, ,			
C <sub>m</sub> H,	1-Deceme	-	0	_	0			۲,			۰ ۵	0 0	۰ ،	0 0	0 0	0 0	120.56423	120.74240	0.00065
ī.	1-Dodecene		۰,	<b>-</b> .	5 (	<b>-</b> .:		>:		» !	<b>&gt;</b> c	h <	> 0	<b>,</b>	> <	> c	20212120	20110.01	30000
	The state of the s		:		:						:	:	:		:	:			

	Ехр. <i>θ</i>			(1,3,2,4eartiene C&CCC) (1,3,2,4eartiene C&CCC) (1,3,4eartiene CCC) (1,3,4eartiene CCC) (1,4,4eartiene CCC) (2,4eartiene CCCC)		118.5 (2-methylpropene)	121 (2-methylpropene)	107 (prepane)	112 (propars) 113.8 (butane) 110.8 (feobritane)	111,0 (butane) 111,4 (isobutane)				110.8 (isobutane)		111.4 (isobutane)	111,4 (isobutne)	
	(a) (c)	118.36	113.84	123.46	118.19	116.31	121.85	108.44	110,49	110.49	109.50	109.44	109.44	110.67	110.76	111.27	111.27	107.50
	e. ©			·	123.46													
	()				11836	·	(16.31											
	, (°)								69.51	15'69		70.56	70,56					72.50
$E_r$ is $E_r(atom - atom, ntsp^3.AO)$ .	<i>E</i> <sub>7</sub> (eV)	0	-1.85836	-1.85836		0	<u>:</u>	O			0			-1,85836	o	0	-1.85836	
(atom - ato	ፚ	1.07647	0.81549	0.81055		1.17300		1.15796		ï	1.15796			0.81549	1.04887	1,04887	1,04887	
Er is Er	ۍ	0.75		<b></b> .		0.75		0,75			0.75			-	0.75	0.75	0.75	
vere used.	ပံ	-	-	-		-		1			_			-	-	1	1	
ling angle v	ប៊	0.75	,	-		-		-			-				0.75	0.75	6.73	
n the preced	C <sub>2</sub>	0.91771	0,81549	0.81549				,			_			0.81549	17710.0	0.91771	17710.0	
meters fron	Starent	0.85252	0.81549	0.80561		0.85252		0.86359			0.86359			0,81549	0.87495	0.87495	0.87495	
tion of $ heta_{r}$ , the para	Atom 2 Hybridization Designation (Table 15.3.A)	-	. 24.	72		æ		. н			. н	÷		52			1	
n the calcula	Eradonike Atom 2	-14.82575 C,	-16.58411 C.	.16.68411 C.	·	Έ		н			=			-16.68412	-14 62573 C <sub>3</sub>	-14.82575 C.	-14.82575 (°,	
ental values [1].	Atom f Hybridization Designation (Table 15.3.A)	6	34			٠		7			7			25	s	3	\$	
and experin	Erminate Aire I	.15.95954	-16.63411 C,	-1688873 C,		.15.93955		-15.75493			-15.75493			-16.68412 (' <sub>k</sub>	 (.°	-15,55033 C.	15.55033	
alkenes	2c' Torniasi Alivus (a <sub>b</sub> )	4.2895	4,795B	4.7539		3,4756		3,4252			3.4252			4,7958	4.1633	4,1633	4.79SB	
meters o	ÄĴĝ	2.86175	2.86175	2,86175		2,04578		2,11106			2.09711			2.91547	נבנוו ג	2.09711	2,90327	
d angle para	2c' Rend 1 (a,)	211323	2 86175	12052		2.04578		2.11106			2.09711			2.91547	2.91547	2.91547	72:00:2	
Table 15.20. The bond angle parameters of alkenes and experimental values [1]. In the calculation of 9, the parameters from the preceding angle were used.	Alums of Angle	$(C_{r}(H)C_{r}=C_{r})$	(c'(c')c' = c')	(כ'=ט'כ') ענ'כ'נ'	,5',3H7	ZHC,H $(H,C,=C,C,)$	(H'C' = C'C')	Mativhens ZHC, H	לנ"נ".	н", С'Н	. Methy! ZHC",H	ZC,C,C,	H,7,22	۳. کر."در" حرر "در" در"	رد: در" H جز: در" H	ZC,C,H In C,	רני"כ" דני"כ"כ"	"כנ"נ"נ"

ALKYNES 
$$(C_n H_{2n-2}, n = 3, 4, 5...\infty)$$

The straight and branched-chain alkynes,  $C_nH_{2n-2}$ , have at least one carbon-carbon triple bond comprising a functional group that is solved equivalently to the triple bond of acetylene. The triple bond may be bound to one or two carbon single bonds that substitute for the hydrogen atoms of acetylene. Based on the energy matching of the mutually bound C, these C-C-bond MOs are defined as primary and secondary C-C functional groups, respectively, that are unique to alkynes. In addition, the corresponding terminal CH of a primary alkyne comprises a functional group that is solved equivalently to the methylyne group of acetylene as given in the Acetylene Molecule section.

The alkyl portion of the alkyne may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkynes are equivalent to those in branched-chain alkanes.

The solution of the functional groups comprises the hybridization of the 2s and 2p

20 AOs of each C to form a single 2sp³ shell as an energy minimum, and the sharing of electrons between two C2sp³ HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. E<sub>T</sub> (atom – atom, msp³.AO) of the C ≡ C-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of acetylene, -3.13026 eV, given by Eq. (14.342). E<sub>T</sub> (atom – atom, msp³.AO) of each -alkyl-bond MO in

25 Eq. (15.52) is -1.85836 eV or -1.44915 eV based on the energy match between the C2sp³ HOs corresponding to the energy contributions equivalent to those of methylene, -0.92918 eV (Eq. (14.513), or methyl, -0.72457 eV (Eq. (14.151)), groups, respectively. For the C-C groups each, comprising a C single bond to C ≡ C, E<sub>T</sub> (atom – atom, msp³.AO) is -0.72457 eV based on the energy match between the C2sp³ HOs for the mutually bound C of the single and triple bonds. The parameter ω of each group is matched for oscillation in the transition state based on the group being primary or secondary.

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The symbols of the functional groups of alkynes are given in Table 15.21. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkynes are given in Tables 15.22, 15.23, and 15.24, respectively. The total energy of each alkyne given in Table 15.25 is calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.24 corresponding to functional-group composition of the molecule. The bond angle parameters of alkynes determined using Eqs. (15.79-15.108) are given in Table 15.26. Each C of the  $C \equiv C$  group can further bond with only one atom, and the bond is linear as a minimum of energy as in the case of acetylene.

Functional Group	Functional Oronin
CC triple band	Gradp symbol
C single bond to C & C (1º)	(i) ./ -(.)
C single band to C = C (2°)	
CH (terminal)	
CH, group	C-H (CH,)
CH, group	(RJ)H-J
CH (alkyl)	(1.1.)
CC bond (n-C)	
CC bond (iso-C)	(a) (c) (c)
CC bond (tert-C)	(a) (b)
CC (iso to iso-C)	3 5
CC (tra t-C)	
CC (r to iso-C)	(a) 3- 3

C = C (4)         C = C (1)         C = C (1) <t< th=""></t<>
C = C         C = C <th< td=""></th<>
C = C = C (-C (i))         C = H (i)         C = H (iI)         C = H (iII)         C = H (iIII)         C = H (iIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII
C = C   C = C   C = C   C = C   C   C
C = C
C = C   C = C   C = C   C = C   C = C     C = C   C = C   C = C     C = C   C = C   C = C     C = C   C = C   C = C     C = C   C   C     C = C   C   C     C = C   C     C = C   C   C     C = C   C   C     C = C   C   C     C = C   C   C     C = C   C   C     C = C   C   C     C = C   C   C     C = C   C   C     C = C   C   C     C = C   C   C     C = C   C   C     C = C   C   C     C = C   C   C     C = C   C   C     C
C = C   C - C (ii)   C - H (i)   C - H (i)     Group   Group   Group   Group     (1.28714   1.99183   1.99185   1.48719   1.64920     1.13452   1.41133   1.41133   0.99572   1.04856     1.20072   1.49569   1.49569   1.05383   1.10974     1.203   (1.450   1.450   1.060   1.0074     (2.4-heandiyme)   (2.4-heandiyme)
Group   CC' (i)   CH' (i)     Group   Group   Group   Group     (1.28714   1.99183   1.99183   1.48719     1.13452   1.41133   1.41133   0.99572     1.20072   1.49569   1.4556   1.0560     (1.203   1.450   1.450   1.060     (2.4-heandiyme)   (2.4-heandiyme)   (2.4-heandiyme)     0.60793   1.4057   1.10466
C = C
C = C
C # C Group (1.28714 1.13452 1.20072 (1.205 (2.4-bendsyme) (2.4-bendsyme)
C # C Group (1.28714 1.13452 1.20072 (1.205 (2.4-bendsyme) (2.4-bendsyme)
a (a,) c (n,) Bond Length Sep. Bond Length (A) h.c (a,)

H - "355.h		E.	E	E.	6.	Final Total	,,	1,41	[ E(C2.p")	$E(C2x\sigma)$	.6	9	9	Ó	Ġ,
RC,C,C, -H		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(cV) Bond 4	Energy C2sp³ (eV)	(°)	(a,	(eV) Final	(eV) Final	€ .	· ©	· ©	( <b>'</b> e)	. <u>e</u>
11 12 13 17	٠٠	-1,54513	6	c	٥	-153,1MM2	17710.0	0.83008	-16,39088	-16.20002	20,99	10.08	48.71	0.98144	0.01428
H, JE, J, J	ن	-1,56513	-0.36229	٥		1133,54311	0,91771	0.81213	-16.7317	-16.36231	(37.17	42.83	65.25	0CRESTO	0.59562
C,C, = C,H	ئ	-1.56513	۰	c	•	-153,18082	17710.0	0.83008	-16.30088	-16.20002	187.91	42.09	66.24	0.51853	0.61599
C, -C, =C,H	۳	4,3622	-0.92918	0	0	152,90716	17710,0	0.54418	-16,11722	-15.92636	17.27	6Z'701	35.39	1.61974	0.20541
C - H (CH <sub>3</sub> )	Ü	#1020.0-	U	c	۵.	152,54487	ודדופס	088980	-15.75493	10195 51-	CP'17	15201 .	41,48	1.23564	0.18708
C - H (CH,)	U	41.92918	#1626'0"		o	-153,47406	17710.0	0.81549	-16,68412	-16,49325	68,47	£\$11.1	35.84	1.35486	0.20933
C-H (CH)	ن	40.9291K	*It26.0-	A1929.1R	•	-154,40324	17716.0	0.77247	-17.61330	-17,42244	61.10	118,50	31.37	1,42,988	0.37326
H,C,C,H,CH, (C,-C, (a))	ű,	#1(ZC)	٥	c		-152.54487	17716.0	0.16359	-13.75403	-15,56407	29'09	116.18	30.08	1.83879	901810
H,C,C,H,CH, - H,C,C,H,CH, -	ú	#](26'0F	H1626'0-	0	0	-153,47406	ונגוניס	0.81549	-16.68412	-16 49325	36,41	123.59	2606	1,90890	0,45117
$R-H_1C_sC_s(H_1C_s-R)HCH_1-$ (C - C (b))	ئ	ALUZUIK	RIGZG'a-	# I(4ZG*0+	c.	154,40324	17716.0	0 772.47	17,61330	-17,42244	48.30	02.161	21.90	1.97162	8.8615.0
$R = H_1C_s(R' - H_1C_s)C_s(R'' - H_1C_s)CH_1 - (C - C'(c))$	ť	#16Z6'0-	.0.72JS7	-0.72457	-0.724S7	07812.451.	17716.0	0,758.89	-17.92866	611.51.11.	48.21	62'161.	21.74	1.95734	0.50570
kaC <sub>2</sub> C <sub>2</sub> (H <sub>1</sub> C <sub>2</sub> - R')HCH <sub>2</sub> ~ (C - C (d))	ŭ	Aluzua.	.0.U2511#	#liczca-	0	-154,40324	177100	0.77247	-17,6[330	-17.42244	# 30 *	07.161	21.90	1,97162	0.51388
$lenC_s(R^- + H_sC_s)C_s(R^- + H_sC_s)CH_s - (C - C_s(e))$	5)	£\$172£'0"	.0.72457	15127.0-	-0.72457	-(54.51399	0,91771	0,76765	-17.92866	675571-	\$0.04	96'621	9911	Cyrrs'1	0.49298
$ler(C,C,(H_1C,-R')HCH_1-(C-C,(9))$	10	T842T.0-	. #1626'O-	#1620.0-	9 ·	-(54.19863	1,11,10,0	. 0.781.55	-17,408.69	-17.31783	. 27.25	22,751	24.04	1,9243	0.47279
$L(C-C, (f))$ $C_{\bullet}(R'-H_1C_{\bullet})CH_1-C_{\bullet}$	ڻ	41.73457	-0.72457	-0,72457	-0.72H57	-154.51399	17716.0	6,76,765	17.92866	617.51.71.	¥0'0\$ -	129.96	22.66	1,94472	86767'0

Parametere													
	C = C Group	Group Group	Group	Coup Group	Group	Group	C-H (ii)	C~C (a)	(4) C + C (9)	(c) (c) (c) (c)	(d) Groun	C-C (e)	C-C (f) Group
$n_1$	3	-	-	-	~	2	-	-	=	_	-	-	-
$n_2$	0	٥	0	0	2	_	0	0	<u>.</u> e	•		-   -	.   c
$n_i$	0	0	0	0	.0	0	0		0	0	.   -	,   -	
۲'	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	Š	0.0	, 0
ς,	-	-	_	-	-	_	_	-	-	-	-	-	3 -
ני	_	-	-	-	-	-	-	-	-	-	-	-	
c <sub>2</sub>	17716.0	0.91771	0.91771	0.91771	17716.0	17716.0	0.91771	17716.0	0.91771	17710	17710	17710	0 91771
ပ်	2	-	1	0	0	-	-	0	0	0	-	-	0
6,	9	2	2	-	-	1	-	2	2	2	2	2	2
	0	٥	0	-	3	2	1	0	٥	٥	0	0	0
C,	0.5	0.5	0.5	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
ين ا	-	_	-	-	-	1	-	Η.	_	-	-	-	-
V, (eV)	-182.53826	-31,29307	-31.29307	-40.62396	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.101.12
V, (eV)	35.97770	9.64042	9.64042	13.66428	38.92728	25.78002	12.87680	9.33352	9,33352	9.37273	9.33352	9.37273	9.37273
/ (eV)	70.90876	7.85528	7.85528	13.65796	32.53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V. (eV)	-35.45438	-3.92764	-3.92764	-6.82898	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3,45250	-3.45250
E(wino) (eV)	-16.20002	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
DEning (ev)	0	-0.72457	-0.72457	-3.130269	0	0	0	0	0	0	c	0	٥
$E_r(Louin)$ (eV)	-16.20002	-13.91032	-13.91032	-11.50462	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
$E_{\Gamma}(\mu, i, o)$ (eV)	-94.90616	-31.63533	-31.63533	-31.63532	-67.69451	-49.66493	-31,63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_r(atom - atom, msp^3.AO)$ (eV)	-3.13026	-0.72457	-0.72457	.0	0	0	С	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_r(\iota x)$ (eV)	-98.03637	-32.35994	-32.35994	-31.63537	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33 08452	-33 08457
ω (10 <sup>13</sup> rad / s)	20.0186	10.3988	17.5426	30.8370	24.9286	24.2751	24.1759	9.43699	.9.43699	15.4846	9 41699	9 55643	£ 7955 6
$E_{K}$ (eV)	13.17659	6.84470	11.54682	20.29747	16.40846	15.97831	15.91299	6,21159	621159	10.19220	621159	6 29021	6 29071
$\vec{E}_{o}$ (eV)	-0.23468	-0.16749	-0.21754	-0.28197	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	0.16416	D 16416
$ec{E}_{ m Kar}$ (eV)	0.27773 [9]	(6) (6)	0.08989 [9]	0.35532 Eq	0.35532 Eq.	0.35532 Eq.	0.35532 Eq.	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312
E. (aV)	-0.09581	-0.12255	-0.17260	-0.10430	-0.22757	-0 14502	-0 07700	0 10150	70700	70051 0	030010	02001.0	0000
$\mathcal{E}_{n_{M_{N}}}(aV)$	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0 14803	0 14803	0.14803	0.10200
$E_{r}(\omega_{mr})$ (eV)	-98.02775	-32.48249	-32.53254	-31.73967	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33 24376	-33 59732	-33 18712	-33 18712
Emm (c. villo) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14 63489	-14 63489
Eneral (c. 101110) (eV)	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	0	0	0	0	0	٥
$E_{D}(iowe)$ (eV)	10.21841	3.21271	3.26276	3.50634	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3,62128	3.91734

The energy parameters (eV) of functional groups of alkynes.

ml values (2).	-C (d) C-C (e) C-C (f) Calculated Experimental Relative Error		29,40432	41,55495	0 0 0 102.3755 102.3557 -0 00011	
imposition and the energies of Table 15.24 compared to the experimenta	$(H_2 - (H_1)) = (-(H_1) - (-(H_2)) = (-(H_2) - (H_2))$				0 0 9 0 9	
C = C ('-(' ('-(' ('-(' ('H')))	(i) (ii)	0 -	- 0 -	- C		
Pormula Name			C.H. J. D. C.H.	Cylin I-Noryne		Takla 16 36 Th. t. 1

												,	•	0	102.37552	2	102,35367	1367	-0,00021
Table 15.26. The bond angle parameters of alkynes and experimental values [1]. In the calculation of $\theta$ , the parameters from the preceding angle were used. E, is E, atom non-atom non-	ond angle p	ammeters	of alkyne	s and experi	imental values [1].	In the calcul	ation of $\theta$ , the par	rameters fro	om the prece	ding angle 1	vere used.	E, is E,	atom – ato	m.msp3.AO).					
	2c'	2c' Denul 1 ( u <sub>0</sub> )	2c. Tembrai Akwa: (a <sub>0</sub> )	Ann I	Atom I Hybridization Designation (Table 15.3 A)	Communication Above 3:	Atom 2 Hybridization Designation	C <sub>3</sub>	Atom 2	ر'	5	ď	25	E, (eV)	9)	0°.	g (°)	Cal. 0	Exp. 6
(C,C, = C,H)							( Page 13.1.A)										+		
Meshi lana ZHC, H	2.11106	2.11106	3,4252	-15.75493	1	Ξ	Ξ	0.86359	-	-	-	0.73	1.15796	6		+			101
				L										,			_	108.44	(propare)
*3*3*37															69.51			. 110.49	(propane) 113.8 (butane)
	L																		(isobutane)
H'5'37															15.69		_	110.49	(butane)
Methy H	2.00711	2.00711	3.6252	-15 75401							1	1				1		_	(isobutune)
70,00						-	=	0.86359	-	-	-	0.75	1.15796	0			_	05.601	
H':5'27															70.56		<u> </u>	109.44	
70,0,07	L	L	-	-16.68412		16,09,11					1				70.56		Ē	109.44	
j. C.	291547	2.91547	4.7958	ڻ ڻ	ສ	,	ĸ	0.81549	0.81549		-	-	0.81549	-1.85836		_	-	110.67	110.8
ZC,C,H in C,	2.91547	2.91547 2.11323	4.1633	-15,55033 C.	s	-14.82575 C.	-	0.87495.	0.91771	27.0	-	6.73	1.04887	0		+	+-	ž, ot.	(isofutane)
H'5"37	7 01547	3 00011		-15.55033		-14.82575			1		†	1	1		1	1	:		
, T. C.		4.1033		ن٠	n	ئن*	 	0.87495	0.91771	57.0	-	0.75	1.04887	•			_	111.27	11.4
70°0'57	2.90327	7,509,27	4.7958	-15.55033 C.	5	-14.12573	-	0.87495	122160	, E	-	1	1		+	+		_	(isobutane)
7C,C,C,						3.		1	+		-	┪	1,04887	-1.53836			=	111.27	(isobutane)

ALKYL FLUORIDES 
$$(C_n H_{2n+2n} F_m, n=1,2,3,4,5...\infty m=1,2,3...\infty)$$

The branched-chain alkyl fluorides,  $C_n H_{2n+2-m} F_m$ , may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein 5 at least one H is replaced by a fluorine. The C-F bond comprises a functional group for each case of F replacing a H of methane in the series  $H_{4-m}C-F_m$ , m=1,2,3,4, and F replacing a H of an alkane. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the C-F functional groups comprises the hybridization of the 2s and 2p AQs of each C to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the F AO to form a molecular orbital (MO) permits each participating orbital to decrease in radius and energy. In alkyl fluorides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), and the F AO has an energy of  $E(F) = -17.42282 \, eV$ . To meet the equipotential condition of the union of the C-F  $H_2$ -20 type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the C-F-bond MO given by Eqs. (15.68) and (15.70) is

$$c_2\left(C2sp^3HO \text{ to } F\right) = \frac{E\left(C, 2sp^3\right)}{E(F)}c_2\left(C2sp^3HO\right) = \frac{-14.63489 \text{ eV}}{-17.42282 \text{ eV}}(0.91771) = 0.77087 \quad (15.110)$$

 $E_T(atom-atom, msp^3.AO)$  of the C-F-bond MO in Eq. (15.52) based on the charge donation from F to the MO is determined by the linear combination that results in a energy that is a minimum which does not exceed the energy of the AO of the F atom to which it is energy matched.

The symbols of the functional groups of branched-chain alkyl fluorides are given in Table 15.27. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl fluorides are

given in Tables 15.28, 15.29, and 15.30, respectively. The total energy of each branched-chain alkyl fluoride given in Table 15.31 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.30 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^5$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(Group)$  (eV) values based on composition is given by Eq. (15.58). In the case of trifluoromethane,  $E_{mag}$  is positive since the term due to the fluorine atoms cancels that of the CH group. The C-C bonds to the CHF group (one H bond to C) were each treated as an iso C-C bond. The C-C bonds to the CF group (no H bonds to C) were each treated as a tert-butyl C-C.  $E_{mag}$  was subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl fluorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.110) are given in Table 15.32.

Table 15.27. The symbols of functional groups of branched-chain alkyl fluorides.

Functional Group	Group Symbol
CF of $CF_m H_{4-m}$	C-F (i)
CF of $C_n H_{2n+2-m} F_m$	C-F (ii)
CH <sub>3</sub> group	$C-H(CH_3)$
CH₂ group	$C-H\left(CH_{2}\right)$
СН	C – H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

מנוכ ו 2.26, דווכ בכטווכון וכמו טטוט ומיתיוכיכי עי טייייי			í		١					1,70	
() ½ - C		C-F (ii)	( 1.3) #	(HJ) H - J	H)	(a)	(a) ::-::	(3)	(a)	(e) (-)	(£)
Group		Group	Group	Group	Group	Group	Group	Group	Group	Group	Стопр
1.72139	_	1,72139	1.64920	1,67122	1.67465	2.12499	2,12499	2.107.25	2.12499	2.10725	2.10725
1.31202	_	1,31202	1.04856	1.05553	1.05661	1.45744	1,45744	1.45164	1,45744	1,45164	1.45164
1.38858		1.38858	1.10974	1,11713	1.11827	1.54280	1.54280	1.53635	1,54280	1.53635	1.53635
	L		1.107	1,107		1,532	1.532	755.1	1.532	1.532	1.532
1382	_	1.382	ş	(C - H propane)	1.122	(propane)	(propane)	(propane)	(propane)	(propane)	(propane)
ide)	<u>-</u>	(methyl fluoride)	1111	1113	_	1.531	1.531	1,531	1531	1.531	153.1
	·		ច្ច	(C-H butane)		(butane)	(butane)	(buttue)	(butane)	(butane)	(butane)
1.11435	ļ	1.11435	1,27295	1,29569	1.2992.4	1,54616	1.54616	1.52750	1.54616	1.52750	1.52750
0.76219		0.76219	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

of branched-chain alkyl fluorides. R,R',R" are H or alkyl groups. $E_r$ is $E_r\{ann-ann,myr^1\mathcal{A}O\}$ .	
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Table 15.29, The MO to HO	
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Tabi	I
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								$(a_{\circ})$	0.15714	0.15714	81160.0	0.15714	0.18708	0.29933	0.37326	901210	0.45117	0.51388	0.50570	0.51388	0.49298	0.47279	0.49298
								d, (a,)	1,15488	1.15488	1,21483	1.15488	1738et	1.35486	1,42911	62868.1	1.90890	1,97162	1,95734	1,97162	1.94462	1,92443	1,94462
('-(') Group	2.10725	1.45164	1.53635	1.532 (propane) 1.531 (butane)	1.52750	0.68888		(•)	47.86	47.16	45.11	47.16	41.48	35.84	31.37	30.08	26.06	21,90	21.74	21.90	2266	24.04	22.66
		54	35					(°)	79.13	27.25	82.98	19.23	102.51	111.53	118.90	116.18	123.59	131.70	131.79	131.70	129.96	127.22	129.96
C-C (c)	2.10725	1,45164	1.53635	1.532 (propane) 1.531 (butane)	1.52750	0.68888		.θ	100.77	100.77	20:16	1001	69'11	CP'89	61.10	28'09	36.41	48.30	48.21	48.30	\$0.04	52,78	50.04
C-C (d) Group	2.12499	1.45744	1,54280	1,532 (propane) 1,531 (butane)	1.54616	0.68600		E(C:2sp²) (eV) Final	-15.98435		-16,91353		-15.56407	-16.49325	-17.42244	-13.56407	-16.49325	-17.47244	67757.71-	-17.42344	677.77.	.17.21783	-11.73779
C-C (c) Oroup	2.10725	1.45164	1.53635	1.532 (propane) 1.531 (butane)	1.52750	0.68888	ر) مد <sub>ن</sub>	Erador (eV) Final	16.17521	-16,17521	-17,10440	-16.17521	-15.75493	-16,68412	-17,61330	-13.75493	-16,68412	-17,61330	-17,92866	-17,61330	-17.92866	-17.40869	-17.92866
-	2.1				-		Er is Er (alom - alam, myp' AO)	(a,)	0,84115	0.84115	0,79546	0.84)15	0.86359	0.81549	0.17247	0.86359	0.81549	0.17247	0.75889	0,77247	0.76765	0.78155	0 76765
ر. – در (a) Group	2,12499	1.45744	1.54280	1.532 (propane) 1.531 (butane)	1.54616	0.68600		(0,	17719.0	0.78069	0,91771	0.78069	0.9177I	0.91771	0.91771	17719.0	17719.0	0.91771	0.91771	17716.0	17716.0	17116.0	171710
C-C (a) Group	2.12499	1.45744	1.54280	1,532 (propane) 1,531 (butane)	1,54616	0.68600	or alkyl groups.	Final Total Energy (.2sp² (eV)	-152,96515		-153.19433		-152,54487	-153,47406	-154,40324	-152.54487	-153,47406	-154,40324	-154.71860	-154.40324	-154.51399	-154,19863	-154,51399
	1.67465	199	827	i.122 (isobutane)	1.29924	560	T.	6.7 (e.V) Bond 4	٥	0	٥	a	•	0	٥	0	٥	•	.0.72457	c c	-0.72457	۵	-0.72457
mental va	1.67	1.05661	1.11827			0.63093	/ fluorides. //	'C, (eV) Bond 3	•				•	o	-0.92918	0	٠.	-0.92918	-0.72457	.0.92918	-0.72457	.0.92918	-0.72457
c' – H (CH <sub>1</sub> ) Group	1,67122	1.05553	1.11713	1,107 (C-H propane) 1,117	1.29569	0.63159	nched-chain alky	(eV) Bond 2	•	·	-0.92918		c	-0.92918	-0.92918	•	-0.92918	-0.92918	-0.72457	-0.92018	-0.71457	-0.92918	-0.72457
Table 15.28. The geometrical bond parameters of branched-chain alkyl fluorides  Parameter $C - F(i)$ $C - F(ii)$ $C - H(iH, )$	1.64920	1.04856	1.10974	1.107 (C-H propane) (11.17	1,27298	0.63580	Table 15.29. The MO to HO intercept geometrical bond parameters of branched-chain alkyl fluorides. $R_iR_iR^*$ are	(eV) Bond I	-1.34946	-1,34946	134946	•1 34946	-0.92918	-0.92918	-0.92918	.0.92918	-0.92918	-0.92918	-0.02918	-0.92918	72457 O-	-0.72457	-0.72457
C-F (ii)	1,72139	1,31202	1,38858	1.382 (4 (methyl fluoride)	1,11435	0.76219	unctrical bond p	Atom	ئن	i.	ڻ	ي	Ü	i	Ü	υ <b>'</b>	ť	ď	ť	ť	ť	ಚ	ပံ
bond param	-	_		de) (methy	<del>-</del>	0	intercept gea											4,-	- H.C.)CH.		- 'H.)(');		C,)CH;-
The geometrical $C-F(t)$ Group	1.72139	1.31202	1.38858	1.382 (methyl fluoride)	1.11435	0.76219	The MO to HO									<u>.</u> .	1.5	$R = H_{\mathcal{L}}(C_{\bullet}(H_{\bullet}C_{\bullet} - R))HCH_{\bullet} - (C - C_{\bullet}(b))$	$R = H_2C_2(R^2 - H_2C_2)C_4(R^2 - H_2C_2)CH_2$	isne; c, (H; c, -R') HCH; -	$nertC_{*}(R'-H_{*}C_{*})C_{*}(R'-H_{*}C_{*})CH_{*} - C(C_{*}C_{*})$	$ter(C_{k}(H_{1}C_{k}-R)HCH_{k}-C_{k})$	$ImC_{s}(R-H;C_{s})C_{s}(R^{*}-H;C_{s})CH_{s} - (C-C_{s};0)$
Table 15.28. Parameter	0 (0,)	c. (a)	Bond Length 2e' (A)	Exp. Bond Length (A)	h,c (a,)	u	Table 15.29.	Bond	$H_{L-a}C_{s} - F_{a}$ $(C_{s} - F_{s}(i))$	H, C, -F,	$-H_{\mathcal{L},\mathcal{L},\mathcal{F}}^{F}$ $((:,-F_{\mathcal{L}}^{F}))$	$-H_{i}C_{i}C_{j}F$ ( $C_{i} - F$ (ii))	C-H (CH,)	(-H (CH;)	( C - H (CH)	H,C,C,H,CH, -	H.C.C.H.CH, -	R-H;C,C,(1	R-H;C; (R'-	10-C (d)	1617(" (R-H)	$I_{eff}(C_{*}(H_{1}C_{*}(H_{2}C_{*}(H_{2}C_{*}(H_{3}(H_{3}C_{*}(H_{3}C_{*}(H_{3}C_{*}(H_{3}C_{*}(H_{3}C_{*}(H_{3}C_{*}(H_{3}C_{*}(H_{3}C_{*}(H_{3}C_{*}(H_{3}C_{*}(H_{3}C_{*}(H_{3}(H_{3}C_{*}(H_{3}C_{*}(H_{3}C_{*}(H_{3}C_{*}(H_{3}C_{*}(H_{3}C_{*}(H_{3}C_{*}(H_{3}C_{*}(H_{3}C_{*}(H_{3}C_{*}(H_{3}(H_{3}(H_{3}(H_{3}(H_{3}(H_{3}(H_{3}(H_{3}(H_{3}(H_{3}(H_{3}(H_{3}(H_{3}(H_{3$	$ImC_{-}(R-H_{2})$

	,		É	ξ.	E	. (2)		(0)	こして	9	(E)
	(i) Group	Group	Growip	Group	Group	Group	Group	Group	Group	Group	Group
	-	1	3	2	-	-	-	-	-	1	-
11,	0 .	0	2	1	0	0	٥	0	٥	0	0
n,	0	0	0	0	0	0	0	0	c	0	0
	0.5	0.5	0.75	6,75	0.75	0.5	0.5	2.0	0.5	0.5	2,0
1	-	-	-	1	-	-	-	-	-	-	-
	~	1	-	1	-	-	_	-	-	-	-
	0.77087	0.77087	17116.0	17716.0	17216.0	0.91771	17716.0	0.91771	0.91771	0.91771	17716.0
c,	0	0	0	-	-	0	0	0	-	-	0
5.	2	τ	-	<b>-</b>	-	2	2	2	2	2	7
5.	0	0	3	2	1	O	0	0	0	Б	0
	0.5	0.5	0.75	0.75	0.75	. 0.5	0.5	9.5	0.5	0.5	0.5
	-	-	1	-	-	-	-	-	_	-	-
V, (eV)	-32.02108	-12.02108	-107.32728	-70.41425	-35,12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29,10112
V, (aV)	10.37015	10,37015	38.92728	25.78002	12.87680	9,33352	9.33352	9.37273	9,33352	9.37273	9,37273
(ab)	4600E'6	6,30097	32.53914	21,06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
(eV)	-4.65048	-4.65048	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3,45250
E(w m) (cV)	-14.63489	-14,63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15,35946
ΔΕηνισ (.m.m) (eV)	0	0	0	0	0	0	0	0	0	0	0
1; (n m) (cV)	-14.63489	-14.63489	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15,35946
E. (n. 10) (aV) .	-31.63534	-31.63534	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
E. (dinn - atom, nixp', AO) (eV)	-2.69892	-2.69892	0	o	. 0	-1.85836	1.85836	-1,44915	-1,85836	-1.44915	-1,44915
$E_{\tau}(m)$ (cV)	-34.33429	-34.33429	-67,69450	-49.66493	-31.63537	-33,49373	-33.49373	-33.08452	-33.49373	-33.08452	-33,08452
w (10th rad/s)	24.8506	12.9435	24.9286	24.2751	24.1759	9.43699	669676	15.4846	9.43699	9.55643	9.55643
E <sub>k.</sub> (cV)	16.35707	8.51966	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\vec{E}_{p}$ (eV)	-0.27472	-0.19826	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Ein (UV)	0.13849	11601.0	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0,35532 (Eq. (13,458))	0.12312	0.17978 [4]	0.09944 fs1	0.12312	0.12312	0.12312
E. (aV)	-0,20547	-0.14371	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E. (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Ty (comp) (aV)	-34.53976	-34,47800	-67.92207	-49,80996	-31.70737	-33.59732	-33,49373	-33,24376	-33.59732	-33.18712	-33.18712
E (1, 10 10) (cV)	-14.63489	-14.63489	.14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489
F ( 10 m) (eV)	0	0	-13.59844	-13,59844	-13.59844	0	0	0	0	0	0
E. (a-) (aV)	5.26998	5,20822	12.49186	7.83016	3,32601	4,32754	4.29921	3.97398	4.17951	3.62128	3,91734

Table 15.31. The total bond energies of branched-chain alkyl fluorides calculated using the functional group composition and the energies of Table 15.30 compared to the experimental values [2]. The magnetic energy E<sub>ner</sub> that is subtracted from the weighted sum of the E<sub>1</sub>(+---) (aV) values based on composition is given by (15.58).

ormufa 0	Name	C-F (i) C-F	( - V	(E)	'.Н.	CH,	н.)	(a)	(P)	(9) )-)	C-C (9)	C-C (e)	0-5-0	l.	Calculated	Experimental	Relative Print
						•								ž	Total Bond	Total Bond	
	Tetrafluoromethane	æ	°		٥	0	c	0	0	0	0	0	0	0	21.07992	21.016	100000
	Trifluoromethane	<b>-</b>	•		•	0	-	0	0	0	ь	0	0		19 28198	61.07	00000
	Difluoromethans	~	0		•	-	0	0	0	0	0	c		. c	C10E1 81	000.01	0.00406
C,H,P	1.Fluoropropane	0	-		_	7	0	7						, -,	41 86745	41 805	1000
C,H,F	2-Fluoropropane	0	_		2	0	_	o		0				. 7	41 04014	19617	2000

<u>o</u> ).	(c) (d) (d) (e) (e)		110.53 (flueroform)	110.38	110,3 (1,2-difluoroethane)	110.83 (1,1-difliomethans)	108.44 (propare)	(10.49 (bolme) (10.88 (10.88 (bolme)) (10.88 (bolme))	111.0 (butne) 110.49 (butne) 111.4 (fsobutne)	109.50	109.44	109.44	110.67 (neobulane)	110.76	111.4 (fsobutane)	
нот,тѕъд А	(e)							69.51	69.51		70.S6	35,07				
Table 15.32. The bond angle parameters of branched-chain alkyl fluorides and experimental values [1]. In the calculation of $ heta_c$ , the parameters from the preceding angle were used. E, is E, (ann — arom, msp AO)	6, (eV)		-1,44915		-1.85836		0		69		ō,	6.	-1.85836	0	0	
were used.	٧		0.84115	0.98172	0.79318	1.04687	1.15796			1,15796			0.81549	1.04887	1.04887	
ding angle	<b>5</b> -		-	57.0	_	0.75	27.0			0.73			-	0.73	0.75	
n the prece	ις		-	-	-	_	_			-			-	-	-	
neters from	ن		-	0.75		67.0	-			-			-	67.0	27.0	
of 0, the parar	C <sub>2</sub>		511980	0.78092 (Eq. (15.64))	Q.77087 (Eq. (15.110))	17719.0	-			-			0.81549	0.91771	0.91771	
the calculation	C <sub>3</sub> .		0.84115	0.79346	0.81549	0.87495	0.86159			0,86359			0.81549	0.87495	0.87495	
tal values [1]. In	Aton 2 Hybridization Designation	(Table 15.3.A)	a	4	ts.	-							23	-	<i>=</i> .	
nd experimen	Erana Atom 3		-16.17321 F	-17.42282 I	.(7,42383	-(4.82575 C,	н			Ŧ			-16.68412	-14.82575	-14.82575	-14.82575
ı alkyl fluorides a.	Atom I Hybridization Designation	(Table 15.3.A)	ū	11	13	8	7			2			23	,	σ,	
nched-chair	Erabert.		-16.17521 F	-17.10440 C.	-ناھ 14412	.ts.25033	-15.75493			.15.75493			16 68412	-15.55@3 C.	.15.55033	.15.55033
sters of bra	_	(0°)	43128	3.8987	4,5826	4,1633	3 4252			3.4252			4,7958	4,1633	4.1633	
igle paranı	, 3, 2c.		2.62403	2,62403	262403	211106	211106			111607			191347	2,11333	1.1797.1	
he bond ar	2c' [mal]		2.62403	2,11,106	73816.2	2.91547	211106			1.09711			291547	2 91547	2.91547	
Table 15.32, 7	Alons of Angle		ZFC, F (C, - F (i))	(C, -F (I))	2C,C,F (C, - F (S))	#5'5'H (C; - F	H".H7	'כנ'כ'נ	H*5*37	Methy!	לנ"נ"נ"	H.J.J7	, , , , , , , , , , , , , , , , , , ,	ZC,C,H I= C,	ZC.,C.,H Im C.,	35.35.37

ALKYL CHLORIDES 
$$(C_n H_{2n+2-m} Cl_m, n=1,2,3,4,5... \infty m=1,2,3... \infty)$$

The branched-chain alkyl chlorides,  $C_n H_{2n+2-m} Cl_m$ , may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein at least one H is replaced by a chlorine. The C-Cl bond comprises a functional group for each case of Cl replacing a H of methane for the series  $H_{4-m}C-Cl_m$ , m=1,2,3, with the C-Cl bond of  $CCl_4$  comprising another functional group due to the limitation of the minimum energy of Cl matched to that of the  $C2sp^3$  HO. In addition, the C-Cl bond due to Cl replacing a H of an alkane is a function group. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the C-Cl functional groups comprises the hybridization of the 2s and 2p AOs of each C to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the Cl AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl chlorides, the energy of chorine is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus,  $c_2$  in Eq.

20 (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. Then,  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), and the Cl AO has an energy of  $E(Cl) = -12.96764 \, eV$ . To meet the equipotential condition of the union of the C - Cl  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.52) for the C - Cl-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ Cl\right) = \frac{E(Cl)}{E(C,2sp^3)}c_2\left(C2sp^3HO\right) = \frac{-12.96764\ eV}{-14.63489\ eV}(0.91771) = 0.81317\ (15.110)$$

The valence energy of the carbon 2p is  $-11.2603 \, eV$  and that of the Cl AO is  $-12.96764 \, eV$ . The energy difference is more than that of  $2E_r(C-C,2sp^3)$  given by Eq. (14.151) for a single

bond. Thus,  $E_r(atom-atom,msp^3.AO)$  of the C-Cl-bond MO in Eq. (15.52) due to the charge donation from the C and Cl atoms to the MO is  $-1.44915\,eV$  based on the energy match between the  $C2sp^3$  HO and the Cl AO corresponding to the energy contributions equivalent to those of methyl groups,  $-0.72457\,eV$  (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl chlorides are given in Table 15.33. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl chlorides are given in Tables 15.34, 15.35, and 15.36, respectively. The total energy of each branched-chain alkyl chloride given in Table 15.37 was calculated as the sum over the integer multiple of each 10  $E_D(Group)$  of Table 15.36 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that was subtracted from the weighted sum of the  $E_D(Group)$  (eV) values based on composition is given by Eq. (15.58). The C-C bonds to the CHCl group (one H bond to C) were each treated as an iso C-C bond. The C-C bonds to the CCl group (no H bonds to C) were 15 each treated as a tert-butyl C-C.  $E_{mag}$  was subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl chlorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.111) are given in Table 15.38.

Table 15.33. The symbols of functional groups of branched-chain alkyl chlorides.

Functional Group	Group Symbol
CCl of CCl <sub>m</sub> H <sub>4-m</sub>	C-Cl (i)
CCl of CCl <sub>4</sub>	C-Cl (ii)
CCl of $C_n H_{2n+2-m} Cl_m$	C-Cl (iii)
CH₃ group	$C-H\left(CH_{3}\right)$
CH₂ group	$C - H(CH_2)$
СН	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

able 15.34.	able 15.34. The geometrical bond parameters of branched-chair	d parameters of bran	ched-chain alkyl chi	n alkyl chlorides and experimental values   1	mial values 11.							
Parameter	() ()-0-0	(!) /2-2	(  ) ひ-3	(.H.) H	( HO) H ~ . )		(E)	(e) -:-:	(a)	(g) U-U	(6)	(E)
	Group	Ошпр	Group	Oroup	Oroup	Group	Group	Grasp	Отопр	Стопр	Group	Group
(")	2,32621	2.37026	2,32621	1.64920	1,67122	1.67465	2.12499	2,12499	2.10725	2.12499	2.10725	2.10725
ر (°) د.	1.69136	1.70729	1.69136	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1,45164	1.45164
Bond Length 2c' (A)	1.79005	1.80692	1,79005	1.10974	1.11713	. 1.11827	1,54280	1.54280	1.53635	1.54280	1,53635	1.53635
Exp. Bond		1	1.802	1.107	1.107	1	1,532	1,532	1.532	1.532	1.532	1.532
Cangth	1.785 (axethyl chloride)	I.767 (carbon retrechlorido)	(ethyl chloride)	( <i>C - H</i> propan 1.117	e) (C - H propane)	(isobutano)	(propane) 1.53 l	(propene) 1.531	(propanc) 1.531	(propane) 1.531	(properte) 1,531	(propane)
3			(1.2-dichlorocibane)	(C-H butane	(C-H butane)		(butane)	(butane)	(butane)	(butane)	(bulane)	(butane)
h,c (a,)	1,59705	1.64416	1.59705	1.27295	1.29569	1.29924	1.54616	1,54516	1.52750	1.54616	1.52750	1.52750
,	0.72709	0.72030	0.72709	0.63580	0.63159	0.63095	0.68600	0,68500	0.68888	0.68600	0.68888	0.68888

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Bond	Atom	k; (eV) Bond 1	آئے (ھا) Bond 2	/; (eV) Bond 3	Er (eV) Bond 4	Final Total Energy ('Zy)	[ <u>a</u> ]	(a,	Eradus (eV) Final	E(C2rp²) (ev) Final	. <sub>0</sub> ©	o (C)	e, C	(°,	(°, 1, 1)
$H_{a,a}(\underline{u}, -(T_a, m = 1, 2, 3, T_a + (T_a), m = 1, 2, 3, T_a + (T_a + (T_a + (T_a + T_a), T_a + (T_a + T_a), T_a + (T_a + (T_a + T_a), T_a + $	Ų,	-0.72457		0	e	-132.34026	17719.0	0.87495	-15.35033	-15.35946	69.62	11031	30.00	1,00590	0.3D463
$H_{L_m}C_{\perp} - (T_{\perp}, m = 1, 2, 3, \dots, T_{\perp} - (T_{\perp}, m = 1, 2, 3, \dots, T_{\perp} - (T_{\perp}, T_{\perp}))$	5	40,77457	٠	۰	٥		1.05158	0.87495	-15.55033		69.62	15.011	30.90	86866-1	ENACE O
(c, - c' (fi))	ن	-n,46459	G	a	c	-152.0K028	17716.0	· 0.88983	+£0GZ*51•	-15.0924R	RC 33	113.02	29.87	02520.2	O.Z.IKO I
(נ''כז' נ''כז'	1.3	-0.46459	۰	5	с		1.0515#	0.KR9X3	-15.25034		86.98	113.02	29.87	2.05530	031801
-H-j', j', '-C' -H-j', j', '-C' (ii))	ڻ	-0.72457	-419391#	-	E	-153.26945	17419.0	0.X2562	-16.47951	-16.28K54	63,18	116.82	27.48	2,06384	0,37248
-H <sub>2</sub> C,C, -C1 -H <sub>2</sub> C,C, -C1	٦	-0.72457	0	c	c		1.05131	0.87493	-13.55033		29'69	110.31	30.50	1,99599	0,30463
с-н (сн.)	i	#1029.0-		-	0	-152.54487	17716.0	0.86339	-15.75493	-15.56407	77,49	15.201	41,48	1,23574	0.1X70X
C-H (CH <sub>2</sub> )	i	R1750,0.	4092918	e	c	153,47406	17716.0	0.81549	-16.68412	-16.49325	68.47	(5,11)	35.84	1.35486	0.25933
C-H (CH)	ر	N\$ (¥26,0.	.0 92918	NI020.0-	c	154.41524	17719.0	0.77247	17,61330	.17,42244	61.10	118.90	31.37	1,42988	0.37326
H.f. J., H.g.H.,	∵*	WIUZU,D.	ь	=	0	-152.54487	17719.0	0.86359	-15.75493	-15.56407	63.82	11911	30,08	61258,1	20145.0
H,C,C,H,Z'H,==	ئ	ж1626.0-	ж 1626 О-	0	c	-153.47406	14416.0	0.81549	-16.68412	-16,49325	36.41	65:551	16,06	06806"1	0,45117
κ− <i>Hζ'',</i> ς',(H <sub>2</sub> ς',−R') <i>HCH</i> ;− κ− <i>Hζ'',</i> ς',(H <sub>2</sub> ς',−R')	ئ	\$1026.0-	#1620,C	R1020.0.	c	154,40334	0.91771	0.77247	-17,61330	WCZV()-	ענ 30	02'15)	06'12	29126'1	12(150
$R = H_1C_1(R^2 + H_2C_2)C_2(R^2 + H_2C_2)CH_1 - CC_2(C_2)$	ď	-0.9291x	A 72457	-0.72457	-0.72457	-154.71860	0,91771	0.75189	-17,92866	-17.73719	48,21	62'161	71.74	1.95734	0.50570
('C' ('A, C' - K') HC'H; - ('C' - ('d'))	ť	-0.92918	-41,9291 R	-0.92918	c	-154,40324	0,91771	1ענד.0	-17,61330	-17,42244	48,30	131.70	21.90	29116.1	0.51388
$len''_{(R'-H_2C')}(r_*(R^*-H_3C'_*)CH_3-$	ť	75457.0-	-0.72457	. 724.57 .	1812/187	-134,51399	0.91771	0.76765	-17.92866	ettet.51-	50.04	96'621	23.55	291161	Q.4929R
(c-c' (f))	ڻ	-0.72457	-0.92VIX	.0.92918	૮	-154.19863	0.91771	0.78135	-17.40169	-(721/83	52.78	22.751	24.04	1.92443	0.47379
$lso(\ (R-H_3C_2)C_4(R^2-H_2C_2)CH_3-$	ڼ	-0.72457	-0,72457	-0.72457	-0.72457	9618,481.	0,91771	0.76765	-17,92866	-17.73779	90'U\$	129.96	9977	1.94462	0.49298

Parameters C-CI		./	ひこ	H./	15	H=1)	(1) (1)	(8.)-)	(7)	47.0		9,0
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'n.	٥	0	c	0	۰	0		٥				,
C.	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	50	50	, 6	,   '
ر.*	0.81317	0,81317	0.81317	_	-	-	-	-	-	-	3 -	3 -
<i>c</i> ,	-	-	-	-	-	-	_	-		-		- -
บ้ำ	1	_	_	177160	0.91771	17716.0	17716,0	0.91773	0.91771	177160	001771	122100
ر.	-	-	-	٥	-	-	0	0	0	-	-	
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C,	D	0	0	e	2	_	0	0	0	0		
(;	50	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
(;	0.81317	0.81317	0.81317	1	-	-	-	-	-	_	-	
V, (aV)	-29,68411	-28.95265	-29.68411	-107.32728	-70.41425	-35,12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29 10112
V, (aV)	8.04432	7.96922	8.04432	38.92728	25.78002	12.87680	9.33352	9.33352	9,37273	9.33352	9.37273	9.37273
T (aV)	6.38036	6,10748	6.38036	32,53914	21,06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V (aV)	-3.19018	-3.05374	-3.19018	-16.26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
F.l. w ww] (aV)	-14.63489	-14.63489	-14.63489	-15,36407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15,35946	-15.35946
DE 11, 10, 10) (aV)	-1.44915	-0.92918	-1.44915	0	0	0	0	0	•	0	0	0
1; { to ta} (cV)	-13.18574	-13,70571	-13.18574	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
F. (W. m) (eV)	-31.63536	-31.63540	-31.63536	-67.69451	49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31,63535
1; (atim - alom, mxp'.AO) (cV)	-1.44915	-0.92918	-1.44915	0	O	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1,44915
F, (va) (cV)	-33.08452	-32,56455	-33.08452	-67.69450	49.66493	-31,63537	-33.49373	-33.49373	-33.08452	-33.49373	-33 08452	-33 08457
w (101 rad/s)	7,42995	7,22380	13,0612	24.9286	14.2751	24,1759	9.43699	9,43699	15.4846	9.43699	9.55643	9,55643
/ <sub>κ</sub> (εν)	4.89052	4.75483	8.59708	16.40846	15,97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
$E_{\mu}$ (eV)	-0.14475	-0.14048	-0.19191	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0 16416	21 16416
First (aV)	0.08059 [12]	0.08059	0.09113	0,35532 (Eq. (13,458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12512	0.17978	0.09944	0,12312	0.12312	0.12312
E. (eV)	-0.10445	-0.10019	-0.14635	-0.22757	-0.14502	-0.07200	-0.10359	-0.07326	-0.15924	-0.10359	-0.10260	-0.10260
Ent (aV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E, b (c.V.)	-33.18897	-32.66473	-33.23086	-67.92207	-49.80996	-51,70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
Cuma (t 11 181) (CV)	-14.63489	-14,63489	-14.63489	.14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Emple et ital (cV)	٥	0	0	-13.59844	-13,59844	-13.59844	0	o	0	0	0	0
E., () (eV)	3.77116	3,39496	3.96108	12,49186	7.83016	3,32601	4.52754	4.29921	3,97398	4.17951	3 62128	3 91734

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2	Culture Action		•		>	-	>	0	0	•	0	0	c	-	•	07446 31	937 31	
	CHICAMEDINE	_	•	0	_	0	0	0	•	•				•	>	25776	0.450	6,00499
Ü	Chloroethans	0	0	-	-	-			•	٠.		>	>	0	•	16,26302	16,312	0.00200
CH.C	1-Chloropropane	•					•	۰ د	<b>&gt;</b> (		0	0.	•	0	۰	28.61064	28.571	SE1000-
-			>		-	•	>	-	~	0	0	c	_	c	•	40 7487.		
S	4-Caloropropane	0	0	-	~		_	-				, ,	•	>	,	40.70834	40.72	-0.00112
υ Ή	1-Chlorobutpane	0	•	-	. –		٠.	•	> •	۷,	-	0	0	0	0	40.86923	40.858	-0.00028
C.H.C	2-Chlorobutane		• •			٠.	٠.	>	•	o	0	0	0	0	0	\$2,92604	52 903	D 00044
			•	-	-1	-		0	_	~	6	•	-	•	,			
į	Laloro-2-methylpropane	0	•	-	-	_	_	-	•			•	•	= 1	>	27.07075	27.572	0.000
D, H, J	2-Chloro-2-methylpropane	0	•	-	, ,		٠.	•	> (	•	<b>-</b>	>	0	0	0	52.99860	52.953	-0.0008.5
טייים	1-Chlomonentane						2 4		-	0	_	0	c	0	7	53,21057	53, 191	-0.000 C
D'H'	-Chlom-3-merhylbutane				- ,		۰ د		4	0	0	0	0	0	0	65,08379	65.061	000014
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ひれん	1-Chlorooctane	0	0	_			- 6		۱ د	7 (	<b>.</b>	0	0	٥	0	77,34233	77.313	-0.00038
Christ	1-Chlorododecane	•				÷	> <	- (	- :	0	0	c	0	0	0	101.55684	101.564	0.00007
Chit	1-Chloroccadecane					= •	•	<b>.</b>	= 1	ь	0	0	0	c	0	150,87640	150,202	0,0000
					-		2	٥	_	c	0	0	c	•	•	233 11304		2000

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	Exp. 0	5	(dichlormethme) [11.3 (chkeroform)		109.2 ( DPC JF des charies) 109.8	(manufacture of typ)	(dh) (dhonke) (1) (dkalabanke) (1) (dkalabanka) (2) (12 deklemechane) (12 deklemechane) (13 deklemechane) (14 deklemechane) (16 deklemechane) (16 deklemechane)	1 IR6 (sthyf dilenids)	(sundan) (01	113 (mysse) 113.8 (hulme) 10.18	(hulanc) (hulanc) 111.4 (icelancianc)				ffQ.R (sechdon)		111,4 (Berhatme)	111.4 (isobutuse)	
	<u> </u>	Œ	111.40	111.46	169.50	100 42	1007.61	110 &3	138.2	110.49	110.49	3 25	109 44	19 65	110 67	110.76	2111	111.27	307.33
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		E																	
40)	6,	<u>-</u>				70.56				15.99	15.69		70.56	8				<u></u>	8 12
ngle parameters of branched-chain alkyl chlorides and experimental values (1), in the calculation of $\theta$ , the parameter from the preceding angle were used. $E_i$ is $E_i$ (oran – other map) AO).  2c' 2c' 2c' 2c' 1c E <sub>i</sub> 1c E <sub>i</sub> (oran – other map) AO).  1.2.1	(ac)	-0.9291Я	c	U		4,929 18	c				e			-1.85836		e	-1.85836		
		14716.0	57760.1	1.15786		0 16339	1,00,007	1.15796			1.15796			64518.0	1.04887	18870'1	THREAL		
		-	81.0	67.0		_	87.0	87.9			0.75			-	0,73	5L N	67.5		
		981317 (Eq.(15.111))	עקא נוציעאט טוניצטט	-		(Eq. (15.11))	-	-			-			-	-	-	-		
meters from th	٦		-	67.0	-		-	811	-			-			1	82.0	52'0	67.75	
of 0,, the para	اِ سَ		17518.11	177190	_		01,863.59	a91771	-			-			0 KI 549	17710-0	17719 0	12216.0	
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af values [1]. In	Atom 2 IIs brid badran	(Table 13.3.A)	-	5	=		פ	-	Ξ			=			ก	-	-	-	
red-chain alkyl chlorides and experimental values [1]. In the	į	i	17 TO	12,76764	=		.12.964 7.7	*)	=			=			יוע נאחוז. נ'	-14,12575	-(4,835); (*,	,) 5/525/11-	
	Ather I Ilyheldizelen	Designation (Table 15.1.A)	-	22	,				,						ก		3	3	
ched-chain	Emm	1	יי יי	.16.27490 f'_	-15.75493		.18.78.09. C.	().	70427.2.1-			::XX5.213			יוניטאוז. כי	-15.5903	-(5.53013 C.	,15.58833 EB82.51-	L
rs of bran	2c' 2c' 2c' 2c' Ername [[hellistics   France   hellistics   respectively   hellistics   respectively   hellistics   respectively   hellistics   respectively   hellistics   respectively   respectively	) e	A.Srø9	1.5%1	3425		3.1539	4.1633	3,4252			3,135			1,775R	11931	4.1033	4.775x	
e paramete	7.5	(4,)	3,3071	1,736,71	2,1977.1		3,5(2)	2.11876	2,11,10%			111601			רוצופב	211123	107711	2.93327	
bond angle	. 7	(a,)	1,3407.1	3.11.06	1177912		2,915.17	2,91547	2.1730%			111700£		_	18167	2.91547	2.91547	2.403.27	
Table 15.38. The	.Unes of Jugs:		<u> </u>	((C, -(7) (iii))		((iii) //- (ii)		(C, - C! (iii))		75.50	н'з'.я	H.JHZ	ZC.JC.C.	H",1",17	"." "."(".")		_	יאונ." ענ"נ."נ."	75.5.77

## ALKYL BROMIDES $(C_n H_{2n+2-m} Br_m, n=1,2,3,4,5...\infty m=1,2,3...\infty)$

The branched-chain alkyl bromides,  $C_n H_{2n+2-m} Br_m$ , may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein 5 at least one H is replaced by a bromine. The C-Br bond comprises a functional group for each case of Br replacing a H of methane for the series  $H_{4-m}C-Br_m$ , m=1,2,3, with the C-Br bond of  $CBr_4$  comprising another functional group due to the limitation of the minimum energy of Br matched to that of the  $C2sp^3$  HO. In addition, the C-Br bond due to Br replacing a H of an alkane is a function group. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

The solution of the C-Br functional groups comprises the hybridization of the 2s and 2p shells of each C to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  hybridized orbital (HO) and the Br AO to form a molecular orbital (MO) permits each participating orbital to decrease in radius and energy. In alkyl bromides, the energy of bromine is less than the Coulombic energy between the electron and 20 proton of H given by Eq. (1.243). Thus,  $c_2$  in Eq. (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. Then, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), and the Br AO has an energy of  $E(Br) = -11.81381 \, eV$ . To meet the equipotential condition of the union of the C-Br  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.52) for the C-Br-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2(C2sp^3HO\ to\ Br) = \frac{E(Br)}{E(C,2sp^3)}c_2(C2sp^3HO) = \frac{-11.81381\ eV}{-14.63489\ eV}(0.91771) = 0.74081\ (15.112)$$

The valence energy of the carbon 2p is  $-11.2603 \, eV$  and that of the Br AO is  $-11.81381 \, eV$ . The energy difference is less than that of  $E_T(C-C,2sp^3)$  given by Eq. (14.151) for a single bond. Thus,  $E_T(atom-atom,msp^3.AO)$  of the alkyl C-Br-bond MO in Eq. (15.52) due to the charge donation from the C and Br atoms to the MO is  $-0.92918 \, eV$  (Eq. (14.513) based on 5 the maximum single-bond-energy contribution of the  $C2sp^3$  HO.  $E_T(atom-atom,msp^3.AO)$  of the series  $CBr_mH_{4-m}$  m=1,2,3 is equivalent to those of methyl groups,  $-0.72457 \, eV$  (Eq. (14.151)). For  $CBr_4$ ,  $E_T(atom-atom,msp^3.AO)$  of the C-Br-bond MO in Eq. (15.52) due to the charge donation from the C and Br atoms to the MO is  $-0.36229 \, eV$  (Eqs. (15.18-15.20 and Eq. (15.29) with a linear combination of s=1,  $E_T(atom-atom,msp^3.AO)=-0.72457 \, eV$ 

The symbols of the functional groups of branched-chain alkyl bromides are given in Table 15.39. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl bromides are given in Tables 15.40, 15.41, and 15.42, respectively. The total energy of each branched-chain alkyl bromide given in Table 15.43 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.42 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that was subtracted from the weighted sum of the  $E_D(Group)$  (eV) values based on composition is given by Eq. (15.58). The C-C bonds to the CHBr group (one H bond to C) were each treated as an iso C-C bond. The C-C bonds to the CBr group (no H bonds to C) were each treated as a tert-butyl C-C.  $E_{mag}$  is subtracted for each t-butyl group. In the case of 2,3-dibromo-2-methylbutane,  $E_{mag}$  is positive since the terms due to the two bromine atoms cancel that of the t-butyl and CH groups. The bond angle parameters of branched-chain alkyl bromides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.112) are given in Table 15.44.

Table 15.39. The symbols of functional groups of branched-chain alkyl bromides.

Functional Group	Group Symbol
CBr of $CBr_mH_{4-m}$	C-Br (i)
CBr of CBr <sub>4</sub>	C-Br (ii)
CBr of $C_n H_{2n+2-m} Br_m$	$\dot{C} - Br$ (iii)
CH₃ group	$C-H(CH_3)$
CH₂ group	$C-H$ $(CH_2)$
СН	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Table 15.40	Table 15.40, The geometrical bond parameters of branched-chain alkyl	ad parameters of branc	-	montides and experimental values [	l values [1].								
Parameter	C-8' (i)	C-Br (ii)	C~Br (iii)	(H (CH.)	(H (CH.)	H-:)	C-C (a)	(e) C-C	(e) ()-()	(E) U-U	(e) () ()	(S)	
		. Group	Group	Group	Group	Group	Group	Group	Oronp	Group	Group	Group	
a (a,)	2.49163	2,52509	2,47529	1.64920	1.67122	1.67463	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725	
c. (a)	1.83395	. 1.84622	1.82719	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744 .	1,45164	1,45164	
Bond Length 2c. (2)	1,94097	1.95396	180001	1,10974	1.11713	1.11827	1.54280	1.54280	1.53633	1.54280	(53633	1.53635	
Evr. Bond			1.93	1.107	1.107		1.532	1.532	1.532	1.532	1.532	1.532	
Length	1.933	1.935	(1.1.1-tribromocthane)	(Sime	(C - H propane)	1.122	(propane)	(propane)	(bropane)	(propane)	(propane)	(propane)	
-	(methyl bromide)	(carbon tetrabronside)	1.950		1.117	(isobutane)	1531	1831	1.531	1531	1.531	1531	
<u> </u>			(1.2-dibromocthane)	(C - H butane)	(C-H butane)		(butane)	(butane)	(butane)	(butane)	(butanc)	(butanc)	
b, c. (a,)	1.68667	1.72265	1,66689	1.27295	1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750	
.	0.73604	0.73115	0.73877	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0,68888	

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Table 15	ļ	3
Tab	1	d

<u> </u>	(and the state of			(1.2-dibromocthane)	(C - H butane)	_	(C-H butane)	(aleman)	- <u>Z</u>	(butane)	(butane)	(butane)		(butane)	(butanc)		(butane)
b, c (a,)	1.68667	1.72265	-	1.66689	1.27295	-	1.29569	1.29924	=	1.54616	1.54616	1.52750	æ	1.54616	1,52750	_	1.52750
	0.73604	0.73115		0.73877	0.63580		0.63159	0.63095	9,0	0.68600	0.68500	0.68888	88	0.68600	0.68888	8	0,68888
Table 15.41.	Table 13.41. The MO to HO intercent geometrical bond parameters of bran	rcent geometrical	bond param		ed-chain alkyl	bromides.	ched-chain alkyl bromides. R.R.W. are H or alkyl proups.	or alkyl groups.		E. is E. ( atom - atom, msp. AO).	.40).						
												ľ					
Bond		Atom		(eV)	(eV) Bond 2	ائم (eV) Band 3	(5V) Bond 4	Final Total Encryy ('2sp'	ીંહ	ાં	Final Final	(C2rg²)	. C	ø_©	e. C	, G	g (g
								(eV)				ruge					
H(',-Hr, m=1,2,3. (C,-Br (i))	. m=1.2.3.	· .		U.3622U	G	С	0	-151,97798	17716.0	0,89582	-15,18804	-14,99717	68.10	06:111	20.52	2.16808	0,33413
$H_{**}("_{-}B_{*}, m=1,2,3.$ $(C_{*}-B_{*}(i))$	, m=1,2,3.	H.		40,36229	5	o	0		1.15169	0,89582	-(5,14404		68.10	06'111	25.02	2.16 KCM	0.33413
(C, -Br (ii))			ئ	-0.18114	u	0	6	-[51,79683	17716.0	D.90ccu	-15.00km	-14 81603	66.10	113.90	28.76	1,11357	0,36734
(C, - 8r (ii)		Br		4,18114	o	υ	U		1,13169	0.90%	-15,00689		66.10	1(3.90	24.76	221357	0.36734
(C, - Br (iii))	,	.,		-0.46459	-0.9291R	0	0	-153,00946	0.91771	0.ИЗИК5	-16,21952	.16.02866	62,67	117,33	26.55	יננוגג	RISKED
(C, - Br (iii)	_	Hr		0,46450		0	G		1.15169	D.HRUK3	-13,29034		69.19	110.81	29.93	2.14337	81916.0
C – H (CH,)		(.		-0.9291R	0	0	0	LX215751-	17710,0	0.86359	£6+\$2'\$1*	-15,56407	77.49	12.201	41,48	1,23564	0. IN7ON
C-H (CH3)	(	٠, ١		X10Z0.0-	#19Z9.0-	0	0	153,47406	17716.0	0.81549	21+x9'91-	-16.49325	68.47	111.53	35,84	1.35486	0.20/33
C - H (CH)		,	٠.	-0.929tk	-0.92918	A1.9291R	c	<b>12601-151</b> -	0.91771	0.77247	-17,61350	-17,42244	61,10	118.90	31.37	1,42958	0,37726
H,C,C,H,CH, = (C, -C, (B))	43 <b>–</b>		٠,٠	4.929tk	o	Ð	۵	-152.54487	0.9(77)	0,166359	-15.75493	-15.56407	63.82	116,13	30.08	LESKIN	0.38176
((c, -(, (a)) H, C, C, H, ('H, -	-t,-	J	ر. ۳	A1929.A	0.92913	0	u	-153,47406	1,7116.0	0.81549	-16.68412	-16.49325	\$6.41	123.39	26.06	1,90%30	0.45117
رر. (۹)) در. (۹)	(C-C'(b))		٠,	#10Z6'0	.092918	₩1626.0-	0	-154.40324	17716.0	0,77247	0.6818,71-	+4224.71-	49,30	131.70	21.90	1.97162	0.51348
R-H <sub>1</sub> C. (K'	$R - H_2C_{*}(R - H_2C_{*})C_{*}(R - H_2C_{*})CH_2$ (C - (° (c))	".)c.H.; -	ر. و	N1929.0-	-0.72457	-0.72457	.0.72457	03817.421-	1,4117.0	0.751319	.17,92866	47.73779	48.28	131.79	21.74	1.95734	0.50570
(c. – c. (q)) pag. c. (H jc	(c, = c, (d))	,	ن ن	#10 <u>5</u> 0.0-	# 16Z6 ()-	.0.920fk	U	-154,40324	0.91771	0.77247	05819.71-	-17.42244	48.30	01,161	21.90	1,971@	0.51388
(((.(e))	$(u-u', (u-H_2'))', (u-H_2')' + U'$		ر ,	-0.72457	-0.72457	.0.72457	-0.72457	4154,51399	0.91771	0,7676.5	-17,92866	47.73779	\$0.0¢	96'621	22.66	1.94402	0,49298
(C-C (I)) IEM(."C."(H"C	(כ – כ (נ) וושנ"כ" (H*c.' – נג) אנא" –	3	C, a	-0.72457	-0.92918	.0,929[Я	Ą.	-154,19863	0.91771	0.7#155	.17,40869	- 17.21783	52.78	17.72	34.04	1.9243	0.47279
ixec",(R-H; (C-C'(I))	(כ. – כ. (4) אינא, "(א. – אינא)כ"(א. – אינא)כאי	].	(, a	-0,72457	A72457	-0.72457	-0.72457	-154,51309	0.91771	0.76763	-17.92866	פידנד.רו-	30.04	120.96	32.66	1,944(Q	0,49297
								i									

Parameters C~Br	C-Br	. C-0		*	3	H-3	C-C (a)	C-C (b)	(a) U-U	C-C (d)	C-C (e)	() J-J
	Group Group	(E) Group	Group Guorg	Group	Group	Group	Group	Group	Group	Group	Оточр	Circuit
u <sup>1</sup>	-	-	-	3	7	-	-	-	-	-	_	_
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٦	0.5	0.5	. 0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
63	0.74081	0.74081	0.74081	-	-		-	1	_	-	-	-
,	-	-	-	-	-	-	-	-	-	-	-	-
· ·	-	-	-	0.91771	17716.0	0.91771	0.91771	17716.0	17716.0	17716.0	17716.0	17716.0
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ر:	5.0	0.5	0.5	0.75	27.0	27.0	0.5	0.5	5.0	0.5	0.5	0.5
٠.	0.74081	0.74081	0.74081	1.	1	1	-	-	1	-	-	
V, (eV)	-27.94806	-27.44996	-28.22940	-107.32728	-70,41425	-35.12015	-28.79214	-28.79214	-29.101.12	-28.79214	-29.10112	-29.101.12
V, (aV)	7.41885	7.36953	7,44631	38.92728	25.78002	12.87680	9,33352	9,33352	6,57273	9.33352	9.37273	9.37273
r (eV)	5.60839	5.43544	5.70686	32,53914	21,06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V, (eV)	-2.80419	27.717.2-	-2.85343	-16.26957	-10,53337	16242.5-	3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E[.o no] (cV)	-14.63489	-14.63489	14.63489	-15.56407	-15.56407	-14.63489	-15.86407	-15.56407	-15,35946	-15.56407	-15.35946	-15,35946
ΔE m, m (cV)	-0.72457	-0.36229	-0.92918	0	0	0	0	ď	0	٥	0	0
$E_{\mathbf{r}}(\omega)$ and $(cV)$	-13.91032	-14.27260	-13,70571	-15.56407	-15,56407	-14,63489	-15.56407	-15.56407	9565521-	-15.56407	-15,35946	-15.35946
E, In and (cV)	-31,63533	1-31,63531	-31.63537	-67.69451	-49.66493	-51.63533	-31.63537	-31,63537	-31,63535	-31.63537	-31,63535	-31.63535
E. (atom - atom, nisp? A() (eV)	-0.72457	-0.36229	-0.92918	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1,44915	-1.44915
$E_{\mathbf{r}}(m)$ (eV)	-32,35994	21.99766	-32.56455	-67.69450	-49.66493	-31.63537	-33.49373	-33,49373	-33.08452	-33,49373	-33,08452	-33.08452
a (10" malls)	6.39733	6.27059	6.46864	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9,43699	9,55643	9,55643
	4.21083	4,12741	4.25777	16.40846	15.97831	15,91299	6.21159	621159	10.19220	6.21159	6.29021	6.29021
R. (eV)	-0.13137	-0.12861	-0.13293	-0.25352	-0.25017	-0,24956	-0.16515	.0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Fr. (cV)	0.07575 [14]	0.08332 [15]	0.07575	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 [5]	0.12312 [2]	51521.0 [2]	0.12512 [2]
F. (eV)	-0.09349	-0.08695	-0.09506	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
F (cV)	0,14303	0.14803.	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
1: [time] (aV)	-32,45343	-32.08460	-32.65%1	-67.92207	49,80996	-31.70737	-33.59732	-33.49373	-33,24576	-33.59732	-33,18712	-33.18712
E L 01 18.   (0V)	14,63489	-14.63489	-14,63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489
Exert le vo wat (eV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
f. (pm.) (eV)	3 18365	. 2.81482	3.38983	12 49186	7.83016	10965 5	437754	4 29921	3 97798	170/17	\$67.69	1 91734

To the magnetic energy ordering the functional group composition and the energies of Table 15.42 compared to the experimental values [2]. The magnetic energy $E_{nw}$ that is industracted from the weighted sum of the $E_{p}(nw)$ (ef.) values based on the $E_{p}(nw)$ orders based on the
composition is given by (15.53). Formula Name C.

			l										
	Relative		-0.00566	0.00323	0.00360	-0.00308	-0.00093	-0.00024	-0.00007	0.00047	0.00051	-0.00033	0.00029
	Experiment al	Total Bond Facrey (eV)	11.196	12.919	15.732	27.953	40.160	40.288	63.477	76.634	88.783	100.952	149.573
	Calculated Total Bond	Energy (eV)	11.25929	12.87698	15.67551	28.03939	40,19709	40.29798	61.48143	76,67019	88.82789	100.98559	149,61639
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		12.1	Promomerhane Promomerhane	ā	-		7 3-Dibones 2 methods	<i>i</i> 2	3	1-Bramoocrans	3	-	1
		S. G.	5 5	H	1	a a	CHAN	i i	L. H.	CrHing	CivitaBr	CuHuBr	

Table 13.44. The bond angle parameters of branched-chain alkyl bromides and experimental values [1]. In the calculation of 6, the parameters from the preceding angle were used. E, is 6, atom - atom, mapl. AO. | 20. | 20. | E, and | 10. | E. |

Εκρ. <i>θ</i>	111.2 (methyl bramids) 113.2 (dilvracaethas)	(Arcraofterns)	(dåremmethane)	110 (1.2-diferencedance)	1050 (1,1,147) trumostome) 109.5	(1,1-drimmochan)	(buodout) .	11.2 (propine) (13.8 (butters)	(jesburn)	(brateria)   [1], d	(nobelane)			(unchatana)			(Lechtlens)	(jechalanc)
<u> </u>	11100	10.51	109,50	3		2	10%	67 UI	1	0F-011	55.60	3 6	103.44	29011	1		2	111.27
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e, ©	<del> </del>	$\perp$	_	, S	1	$\perp$		69.51	1	18.51		70.56	70.56				T	
£, (eV)	81626 07	·	c		Sing		•				6			-1.83936	0			-1,85836
<i>'</i> %'	D N9542	1,04487	1.15790		0.86359	7	R.C.				1.15738			0.KIS49	1.04887	Caster		Mari
ij.	-	27.0	67.73		-	31.0					0.75			-	0.75	2,3	:	5
ڻ"	0 740RF (Eq. (15.512))	ח אמאפט נפה נוז נפה	-		0.74081	Harris des					-			-	_	-	-	+
<del>ن</del>	_	4.73	-		-	T-					-			-	6.75	87.0	Ě	
υĴ	D X4392	0.91771	-		0 1663.59	-					-			0.KI3KD	17710,0	17716.0	177170	1
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Hybridizatum Doğumlum (Table 15.3 A)	ći	ž	=		2	=					=			ą	-	-	-	
i i	-15.18904 Rr	-11.81341 Hr	=		HEREIN H	=					=		ועשאוז-	1430538	ئ	-14,83575	-14,20575	
(Alexification Designation (Table 15.1 A)	es	-	-								-		,	:	۰.		-	
į	-ts.tems RF	-13.33033	-(5.7348)		-18.734-93	-15.75493					13.75493	1	יומפשווי	15.53031	ن:	.15 53vtts	-15 55m3	+
(a.)	91100	4,6313	acr s		utr's	3438				_	9	1	i i		4.3633	1 1633	4 7754	$\parallel$
j e	3160711	3 (673)	112mZ		16507	20112				-+-	II.	1	1211.47		D	2.09711	2,911,27	H
15	3 (672)1	2.11 106	11001		191517	2.1186							1.915.17			121127	2,903,7	
	ZhC,hr (C, - hr (i))	ZHC_Hr ((' br (iii))	ZHC.H ZHC.H ((:) - Br (iii))	ZC',C',H, (C', - Br (iii))	((,' - H- (iii))	H"JH7		27.7.12	H'.J.17	Nath	1.57	H.3.37	76.6	H'.J'.17	ن			4.6,0,

ALKYL IODIDES 
$$(C_n H_{2m+2-m} I_m, n=1,2,3,4,5...\infty m=1,2,3...\infty)$$

The branched-chain alkyl iodides,  $C_nH_{2n+2-m}I_m$ , may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds wherein 5 at least one H is replaced by an iodine atom. The C-I bond comprises a functional group for I replacing a H of methane  $(CH_3I)$  or for I replacing a H of an alkane corresponding to the series  $C_nH_{2n+2-m}I_m$ . The C-I bond of each of  $CH_2I_2$  and  $CHI_3$  comprise separate functional groups due to the limitation of the minimum energy of I matched to that of the  $C2sp^3$  HO. The methyl, methylene, methylyne functional groups are equivalent to those of branched-chain 10 alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2CH)$  and t-butyl  $((CH_3)_3C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups that are equivalent to those of branched-chain alkanes.

- The solution of the C-I functional groups comprises the hybridization of the 2s and 2p AOs of each C to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the I AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl iodides, the energy of iodine is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus,  $c_2$  in Eq.
- 20 (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. Then, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E\left(C,2sp^3\right)=-14.63489~eV$  (Eq. (15.25)). The I AO has an energy of  $E\left(I\right)=-10.45126~eV$ . To meet the equipotential condition of the union of the C-I  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.51) for the C-I-bond MO given by Eqs.
- 25 (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ I\right) = \frac{E(I)}{E(C,2sp^3)}c_2\left(C2sp^3HO\right) = \frac{-10.45126\ eV}{-14.63489\ eV}\left(0.91771\right) = 0.65537 \quad (15.113)$$

The valence energy of the carbon 2p is  $-11.2603 \, eV$  and that of the I AO is  $-10.45126 \, eV$ . The energy difference is positive. Thus, based on the maximum charge density on the  $C2sp^3$ 

HO  $E_T(atom-atom,msp^3.AO)$  of the C-I-bond MO in Eq. (15.52) due to the charge donation from the C and I atoms to the MO is -0.36229~eV (Eqs. (15.18-15.20 and Eq. (15.29) with a linear combination of s=1,  $E_T(atom-atom,msp^3.AO)=-0.72457~eV$  and  $E_T(atom-atom,msp^3.AO)=0$ ) for methyl and alkyl iodides, -0.18114~eV for diiodomethane, and 0 for  $CHI_3$ .

The symbols of the functional groups of branched-chain alkyl iodides are given in Table 15.45. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkyl iodides are given in Tables 15.46, 15.47, and 15.48, respectively. The total energy of each branched-chain alkyl iodide given in Table 15.49 was calculated as the sum over the integer multiple of each  $E_D(G_{CPURP})$  of Table 15.48 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that was subtracted from the weighted sum of the  $E_D(G_{CPURP})$  (eV) values based on composition is given by Eq. (15.58). The C-C bonds to the CHI group (one H bond to C) were each treated as an iso C-C bond. The C-C bonds to the CI group (no H bonds to C) were each treated as a tert-butyl C-C.  $E_{mag}$  is subtracted for each t-butyl group. The bond angle parameters of branched-chain alkyl iodides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.113) are given in Table 15.50.

20 Table 15.45. The symbols of functional groups of branched-chain alkyl iodides.

Functional Group	Group Symbol
CI of $CH_3I$ and $C_nH_{2n+2-m}I_m$	C-1 (i)
CI of $CH_2I_2$	C – I (ii)
CI of CHI <sub>3</sub>	C-I (iii)
CH₃ group	$C-H$ $(CH_3)$
CH₂ group	$C-H$ $\left(CH_{2}\right)$
СН	. C – H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

	_								
	() 2-2	Group	2.10725	1,45164	1.53635	LS32 (propane)	(butane)	1.52750	0.68888
	(a) D-D	Group	2.10725	1,43164	. 53621	1.532 (propens)	(butane)	1.52750	O GRRRR
	(g) 2-2	Group	2.12499	1.45744	1.54280	1,532 (prepane)	(butane)	1.54616	0 68600
	(9) 2~2	Group	2.10725	1,45164	1.53635	1,532 (propane)	(butane)	1.52750	0.68888
	(q) J-J	Отопр	2.12499	1.45744	1.54280	(.532 (propane)	(butane)	1,54616	0 68500
	C-C (a)	Group	2.12499	1.45744	1.54280	1.532 (propane)	(butane)	1.54616	0.68600
		Group	1.67465	1.03661	1.11827	1.122	(isoporana)	1.29924	0.63095
values [1].	C-H (CH.)	Group	1.67122	1.05553	1,11713	t.107 e) (C – H propane)	(C-H butane)	1,29569	0.63159
cyl iodides and experimental values [	C-H (CH.)	Group	1.64920	1.04856	1.10974	1.107 (C-H propane)	(C-H butane)	1.27295	0.63580
thed-chain alkyl iodid	(m) /-3	Group	2.70662	2.03222	2.13081	2.15	(cerpon tournouted)	1.78770	0.75083
d parameters of branc	(1) 1-2	Group	2,68865	2.02546	2.14365	2:13	(medica todatoc)	1,76815	0.75334
Table 13.46. The peometrical bond parameters of branched-chain alk	(1)	Group	2.67103	2.01881	2.13662	2.132	fabron trinami	1.74894	0.75582
1 able 13.46.	Paruneter		( a (a,)	c. (a,)	Bond Length 2e* (A)	Exp. Bond Length	3	b,c (a,)	

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.

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Table 13.47. The MO to HO intercent ecometrical bond parameters of branched-chain alkyl indictes. $R,R',R'$ are $H$ or alkyl groups. $E_r$ is $E_r$ ( $Grom-anon,map^2$ - $AO$ )	trical bond	parameters of b	anched-chain al	kyl iodides. R.	R.R. are H or	· alkyl groups.	E, is E, (alom	1- atom, msp.,	( <u>)</u>						
Bond	Atom	E, (eV)	/5, (eV) Band 2	E, (eV) Bond 3	Er (eV) Bond 4	Final Total - Energy (-2xp²)	(a <sub>0</sub> )	'J @	Final Final	E(C2xp²) (eV) Final	·6 ©	(o)	(°)	ď, (ơ,)	(°)
CH,1	U	-0.IN114	G		0	-151.79583	17710.0	0.90664	-15,00689	-14,81503	8769	110.37	29.08	233472	0.31560
(C, -1 (i))	`	-0.18134					1,30183	0.90664	-15.00689		69.63	110.37	29.08	2,33447	03150
()) (')'5'H-	U	-0.18114	-0.92918		0	.152.72602	17716.0	0.83377	-15.53608	-15.74521	63.16	116.14	25.82	2.40436	0.38554
(C, -1 (I))	-	-0.18114	9	0	0		1,30183	0.50664	-15.00589		69.63	110.37	29,08	23342	0.31560
C,H,J; (C, -1 (ii))	ن	-0.09057	٥		0	151.70526	1216.0	0.91214	-14.91632	-14.72546	63.61	111.39	11,115	\$1856.5	מענננ 0
C,H,J,	`	-0.09037	۰	•	0		1,30133	0,91214	-14.91632		68.61	111.39	28.71	2,35818	0,33772
C, H, (ii)	ن	5	b		6	.151,615@	17716.0	17716.0	-14.87373	-14.63489	67.56	112,44	28.32	2,31256	0.33033
C,H,	`	c	a	0			1,30183	122160	-14.92575	14,63489	67.56	112.44	2832	2,38256	0.35035
C-H (CH <sub>1</sub> )	U	.0.92918	0	0	٥	-152.54487	17719.0	0,16359	-15.75493	-13 35407	77.49	102.51	41.48	1,23564	Q.1870R
C-H (CH <sub>2</sub> )	L	-0.92918	NIUZU.D.	0		-153,47406	17716.0	0.81549	-16.68412	-16.49325	68.47	111.53	35.84	1,35486	0.29933
C-H (CH)	L	-0.92918	-0.9291R	4) 9291X	0	154,40324	0.91771	0,77247	-17,61330	-17,42244	61.10	115.90	31.37	1.42918	0.37326
H;C,C,H;CH; -	ن	-0.92918	e	o	0	152.54487	17710.0	0.16359	-15.73493	-15 56407	G3.82	116.18	30.08	1,83879	0.38106
H;C;H;C;H;=	ن	-4,9291ж	#1620.0-	٥		-153.47406	17710.0	0.81549	-16,61413	-16.49328	56.41	65.131	26.06	1.90890	0.45117
$R-H_3C_2(H_3C_4-R)HCH_3-$	i,	-0.9291x	X1620.0.	.0,929 f g	C	-154.403.24	17710	0,77247	-17.61330	-17,42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2C_a(R^2 - H_2C_a)C_3(R^2 - H_2C_a)CH_2 - (C^2 - C^2)C$	Ü	X1626 O-	-0.72457	-0.72457	-0,72457	-154,71860	17719,0	0,75489	-17.92866	971.71.	48.21	631,79	21,74	1.95734	0.50570
(C-C'(d))	ئ	-0,92918	K1620.0-	\$167617	c	-154,40324	0.91771	1\$£17,0	-17,61330	-17.42244	48.30	111.70	21.90	1,97162	0.51388
$(R - H_3C_3)C_4(R^2 - H_3C_3)CH_3 - (C - C^2)C_3$	ت	-0,72457	-0.72457	42457	-0,72457	-154.51399	17710.0	0.76763	-17,92866	.17,73779	50.04	129.26	22.66	1,94462	0.49298
$(e^{-iC}, (H, C, -R)HCH_2 - (C, -C, 0))$	ئ:	-0.72457	K1620.0+	н 1676°U-	ó	-154,19863	17719.0	0.78155	-17.40%60	-17,21783	52.7K	17.73	24.04	1,92443	0.47779
$(\kappa_{1}\kappa_{1})^{2}(K-H_{2}\kappa_{2})C_{1}(K-H_{2}\kappa_{1})CH_{2}-K_{2}\kappa_{1}$	ئن	-0,72457	-0,72457	LSPELIU	72A57.0.	-154.51399	17716.0	0.75765	-17.92866	-17.73779	\$0.04	129.96	. 22.66	1,94462	0.4920R

Parameters	1-3	1~3	/-J	CH,	CH,	H-J	(r) )~_)	(Q) 2-2	(a) 2~2	C-C (q)	(e) C-C (e)	(J) (J) – (J)
	⊕ G	@ <u>B</u>	(E)	Group	Group	Grand	Group	g the b	Group	Group	Grand	Group
1,	]  -	-	-		2	_	_	_	-	_	-	-
'n	۰	0	٥	. 7	-	o	0	o	0	0	0	0
É	۰	٥	0	0	٥	c	0	o	0	0	0	٥
ئ	0.5	0.5	0.5	6.75	0.75	0.75	6.5	0.5	0.5	0.5	0.5	6,5
ن	0.65537	0.65537	0.65537	-	1	-	1	J	-	-	-	-
5	-	-	-		-	-	-	-	-	-	-	-
£.	-	-	_	0.91771	17719.0	0.91771	12416'0	17116.0	17710	17716.0	17710	17716.0
5	-	0	-	٥	1	-	0	0	0	-	-	٥
'5	7	2	2	-	1	1	2	2	2	2	2	7
6,	0	0	o	n	2	-	o	0	0	0		0
. C.	6.5	9.0	5'0	27.0	0.75	0.75	6.6	0.5	0.5	0.5	0.5	5.0
C.,	0.65537	0,65537	0,65537	-	1	-	1	1	-	-	-	-
V, (aV)	-26.59109	-26.34902	-26.10696	-107.32728	-70.41425	-35.1201.5	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (cV)	6.73951	6.71739	6.69505	38.92728	25.78002	12.87680	9,33352	533352	9.37273	9.33352	9.37273	9,37275
T (eV)	4.97768	4.90005	4.82280	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V (eV)	-2.48884	-2.45002	-2.41140	-16.26957	-10.53337	-5.24291	-3.38732	-3,38732	-3.45250	-3,38732	-5.45250	-3.45250
El.w no (cV)	-14.63489	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15,35946
DE 11,200 (cV)	-0.36229	-0.18114	0	0	0	•	0	0	0	0	0	0
Fr (.10 m) (eV)	-14.29907	-14.45375	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15,56407	-15.35946	-15,56407	-15.35946	-15.35946
E, (n, w) (eV)	-31.63534	-31.63535	-31.63540	-67.69451	26799.67	-31.63533	-31,63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
Er (atom - atom, msp',AO) (eV)	-0.36229	-0.18114	٥	0	0	0	-1.85836	-1.85836	-1,44915	-1.85836	-1.44915	-1.44915
Er (200) (cV)	-31,99766	-31.81651	-31.63537	-67,69450	49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33,49373	-33,08452	-33.08452
(10 <sup>15</sup> rad/s)	10.2318	5.36799	9.90080	24.9286	1512.42	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E <sub>K</sub> (eV)	6,73472	3.5331	6.51688	16,40846	18,97831	15.91299	6,21159	621159	10.19220	6.21159	6.29021	6.29021
E, (eV)	-0.16428	-0.11832	-0.15977	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$ec{E}_{ m K  o B}$ (eV)	0.06608	0,06608	0.06608 [6]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 (2)	0.17978 [4]	0.09944	0.12312	0.12312 [2]	0.12312 (2)
E. (eV)	-0.13124	-0.08527	-0.12673	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	09701.0-
$E_{-\epsilon}(eV)$	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Er (n-1 (aV)	-32.12889	-31,90179	-31.76210	-67.92207	-49,80996	-31.70737	-33.59732	-33,49373	-33,24376	-33,59732	-33.18712	-33.18712
Emans (a. wound) (aV)	-14,63489	-14.63489	-14,63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489
E (1, .0:10) (aV)	0	0	0	-13.59844	-13,59844	+13.59844	0	D	0	0	0	0
Ep (roun) (aV)	2,71108	2.63201	2,34429	12,49186	7.83016	3.32601	432754	12662'\$	3.97398	4.17951	3.62128	3.91734

Table 15.4	Table 15.49. The total bond energies of branched-chain alkyl lodides calculated us	of branched-chain	alkyl iodides	calculated using	g the function	moo dnad r	sosition and the	encryics of T	Table 15.48 co	enpared to the	: exponimental	values [2]. Ti	ne magnetic en	ergy 🖅 that	is subtracted	from the wei	ghted sure of	Lising the functional yrrup composition and the energies of Table 13.48 compared to the experimental values (2). The magnetic energy $E_{nq}$ that is subtracted from the weighted sum of the $E_{0}(c_{nq})$ (e)
based on c	ased on composition is given by (15,58	18).						i								-		
Formula	Vonc	(i) 1-3	(u) /-2	(ii) C-1 (ii) C-1 (iii)	CH,	$CH_1$	(J) H.J	CH (I)	C-C (a)	(a) 2-2	(e) C-C	C-C (a) C-C (b) C-C (c) C-C (d) C-C (g)	ر-ر (ه)	(j) )-:	E.	Calculated Total Bond	Experimental Total Bond	Relative Error
									-							Energy (eV)	Energy (cV)	
	Triodomelhase	0	c		0	=	-	0	0	•	0	-	0	٥	0	10.33888	10.405	0.00444
	Dilodomethane	٥	~	0	0	<b>-</b>	6		•	•	0	6	•	٥	7	12,94614	12,921	.0,00193
	Iodomethem	-	c	•	-	c	•	0	0	•	Ċ	5	•	0	0	15.20294	15.163	0.00263
	fodocthane	_	0	c	-	-	٥	c	_	•	0	c	۰	۰	•	27,36064	27,343	250000
C,H,I	1-lodopropano	-	c	0	_	7	0	•	7		c	0	•	٥	•	39,51834	32,516	200000
	2-lodopropane	-	c		~	=	-	٥	0	7	0	ø	0	0	•	39,61923	20,00	0,0000
	2-lodo-2-methy laterane	_	-	0	•	=	-	-	-	•		_	-	•	7	51 96057	61 800	00000

											-						
	Exp. θ (•)			1(1.2 (methyl iodife)			107 (propane)	(propunc) (propunc) (13.8 (butanc) (10.8 (isobutane)	111.0 (Dulane) 111.4 (Geobetane)				1.10,8 (sububus)		(fsobutare)	(isobutane)	
	j. ©	112.10	פנגוו	109,50	109.44	111.16	12,20	110,40	110.49	109.50	100.44	100.44	110.67	110.76	111.27	111.27	107.50
	, (•)																
	6 D	_	_								L	L		<u> </u>	<u> </u>		
6	0, D	ļ			70.56		<u> </u>	12.69	62.51		70.56	70.56	ļ				22.0
- aloni, msp'.A	E <sub>r</sub> (eV)	-0.36228	°	o		-0.3K22R	•			٥			-1.85836			-1.85836	
Er is Er (atom	۷,	-	1.0000	1,157%		0,87495	1.13796			1.157%			0.81549	1,04887	1.04847	1.04837	
le were used.	ر.	_	0.75	6.73		-	0.75			6.75			-	0.73	6.73	6.75	
preceding any	ี ("	0.65537 " (Eq. (15.113))	0,76815 (Eq. (15.65))	-		0,65537 (Eq. (15.113))	-							-	-	-	
neters from the	<del>ن</del>	-	67.0	-	ļ	-	-			-			_	0.75	67.0	0.75	
f 0, the param	Amer 2	-	17710.0	_		0.87495	-			1			0.K1549	17710.0	17716.0	0,91771	
e calculation o	C. Arma I	-	17710.0	0 MGU59		0,47455	0,00359			0,86359			0,81549	0.87493	0.87495	0,87495	
values [1]. In th	Alon 3 Hybridication Designation		-	÷		-	π .			<b>.</b>			22	-	1.	1	
experimenta	Am 2	10,45126	32126 1	×		10,45126	н			Ŧ			-16.0H12	-14.82575 C.	-14,82575 C,	-14,X2373 C,	
alkyl todides an	Atom I Hybridization Designation	1	-	-		~	1			1			я	~	~	۶	
iched-chain	Enach Am 1	-10.45126	-14.82575 (',	-15.75493		15,55033	-15.75493			-15.75493			-16,68412 C.	-15.55033 C.	-15.55033 (' <sub>h</sub>	-15.55033	
is of bran	1 1 1 (°)	6,7205	5.2203	3,433		5.7939	3,4252			3,4232			4,7958	4,1633	4.1633	4.795x	
le paramete	(g) [E #	4 03002	4.03763	2.00711		4.03763	211106			11260.5			2.91547	211333	2.09711	2.90327	
e pond and	25°. (a,)	4.05072	2.11106	2 09711		2.91547	2,11106			1,09711			2.91347	2.91547	2,91547	2.90327	
18ble 15.50. He bond angle parameters of branched-chain alkyl todides and experimental Values [1]. In the calculation of 8, the parameters from the preceding angle were used. E, is E, {atom - aton, mrg 'AO}	Viscos of Aspir	(C, -1 (6))	(C, -1 (i))	ZHC,H ZHC,H (C, -1 (0))	(C, -1 (f))	(c,"-1 (i)) 7C,C,1	H.:)H2	מ'נוני	н'.5".⊅	H". H7	7ر. رار.	H"J".	נייני עניניני	יינ" תנ"נ"א	", ™ TC"C"H	*J.€ *#.C*	70°C'C'

## ALKENYL HALIDES $(C_n H_{2n-m} X_m, n=3,4,5... \infty m=1,2,3... \infty)$

The branched-chain alkenyl halides,  $C_n H_{2n+2-m} X_m$  with X = F, Cl, Br, I, may comprise alkyl and alkenyl functional groups wherein at least one H is replaced by a halogen atom. In the case that a halogen atom replaces an alkyl H, the C-X bond comprises the alkyl-halogen 5 functional groups given in their respective sections. The alkenyl halogen C-X bond comprises a separate functional group for each case of X bonding to the C=C-bond functional group given in the Alkenes section. In addition the CH group of the moiety XCH=C comprises a functional group unique to alkenyl halides. The straight and branched-chain alkenes,  $C_n H_{2n}$ , comprise at least one carbon-carbon double bond comprising a functional group 10 that is solved equivalently to the double bond of ethylene. The double bond may be bound to one, two, three, or four carbon single bonds that substitute for the hydrogen atoms of ethylene. The three distinct functional groups given in the Alkenes section are C vinyl single bond to -C(C)=C, C vinyl single bond to -C(H)=C, and C vinyl single bond to  $-C(C)=CH_2$ . In addition,  $CH_2$  of the  $-C=CH_2$  moiety is also an alkene functional group solved in the 15 Alkenes section.

Consider the case where X = Cl substitutes for a carbon single bond or a hydrogen atom. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent fragments, and differences in oscillation in the transition state, two distinct C - Cl functional groups can be identified: Cl vinyl single bond to -C(C) = C and Cl vinyl single bond to -C(H) = C. The alkenyl-halide CH group is equivalent to that solved in the Hydrogen Carbide (CH) section except that  $\Delta E_{H_3MO}(AO/HO) = -1.13379 \ eV$  in order to energy match to the C - Cl and C = C bonds.

The alkyl portion of the alkenyl halide may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) 25 functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkene halides are equivalent to those in branched-chain alkanes.

 $E_T(atom-atom, msp^3.AO)$  of the C=C-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of ethylene, -2.26759~eV, given by Eq. (14.247).  $E_T(atom-atom, msp^3.AO)$  of each C-C-bond MO in Eq. (15.52) is -1.85836~eV or -1.44915~eV based on the energy match between the  $C2sp^3$  HOs corresponding to the energy contributions equivalent to those of methylene, -0.92918~eV (Eq. (14.513), or methyl, -0.72457~eV (Eq. (14.151)), groups, respectively.

The solution of each C-X functional group comprises the hybridization of the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the X AO to form a MO permits each participating orbital to decrease in radius and energy. The alkenyl C-X-bond functional groups comprise single bonds and are equivalent to those of the corresponding alkyl halides except that the halogen AO and the C-X-bond MO are each energy matched to the alkene  $C2sp^3$  HO. In alkenyl halides with X = Cl, Br, or I, the energy of the halogen atom is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus,  $c_2$  in Eq. (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. For example, the hybridization factor  $C_2$  of Eq. (15.52) for the alkenyl C-Cl-bond MO given by Eq. (15.111) is  $C_2(C2sp^3HO to Cl) = 0.81317$ .

 $E_r(atom-atom,msp^3.AO)$  of the alkenyl C-Cl-bond MO in Eq. (15.52) due to the charge donation from the C and Cl atoms to the MO is -0.72457~eV for the Cl vinyl single 20 bond to -C(H)=C C-Cl group and -0.92918~eV for the Cl vinyl single bond to -C(C)=C C-Cl group. It is based on the energy match between the Cl atom and the  $C2sp^3$  HO of an unsubstituted vinyl group and a substituted vinyl group given by Eqs. (14.151) and (14.513), respectively.

The symbols of the functional groups of branched-chain alkenyl chlorides are given in Table 15.51. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of branched-chain alkenyl chlorides are given in Tables 15.52, 15.53, and 15.54, respectively. The total energy of each branched-chain alkenyl chloride given in Table 15.55 was calculated as the sum over the integer multiple of each  $E_D$  (Group) of Table 15.54 corresponding to functional-group composition of the molecule.

The bond angle parameters of branched-chain alkenyl chlorides determined using Eqs. (15.61-15.70), (15.79-15.108) and (15.111) are given in Table 15.56.

Table 15.51. The symbols of functional groups of branched-chain alkenyl chlorides.

Table 15.51. The symbols of functional group	ips of orangineu-chain arkenyr chiorides.
Functional Group	Group Symbol
CI vinyl single bond to -C(H)=C	C-Cl (i)
Cl vinyl single bond to $-C(C)=C$	C-Cl (ii)
CC double bond	C = C
C vinyl single bond to $-C(C)=C$	C-C (i)
C vinyl single bond to -C(H)=C	C-C (ii)
C vinyl single bond to -C(C))=CH <sub>2</sub>	C-C (iii)
CH (alkenyl halide)	C-H (i)
CH₂ alkenyl group	$C-H\left(CH_{2}\right)$ (i)
CH₃ group	$C-H$ $(CH_3)$
CH₂ alkyl group	$C-H\left(CH_{2}\right)$ (ii)
CH (alkyl)	C-H (ii)
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

C-C (f)		2.10725	1.45164	1.53635	1.532 (propane) 1,531 (butane)	1,52750	0.6888
ر – در (e) محمدان		2,10725	1.45164	1,53635	1.532 (propane) 1.531 (butane)	1.52750	0.68888
C-C (d)		2,12499	1762744	1,54280	1.532 (propane) 1.531 (butane)	1.54616	O KRKOO
وanou <u>n</u> ن-د (ه)		2,10725	1,45164	50965'1	1.532 (propane) 1.531 (butane)	1,52750	0.68888
Granb (a) 2-2		2,12499	1.45744	1.54280	1.532 (propane) 1.531 (butane)	1.34616	0.68.600
C = C (s)		2.12499	1.45744	08215"1	1.532 (propane) . 1.531 . (butane)	1,54616	0 68600
C - H (ii) Group		1,67465	1.05661	1:11827	1,122 (snatudosi)	1.29924	161005
C-H (CH <sub>1</sub> )   C-H (CH <sub>1</sub> )   C	(ii) Group	1.67122	1.05553	1,11713	1.107 (C-R propane) 1.117 (C-H	1,29569	051190
C - H (CH <sub>1</sub> )		1.64920	1.04856	1,10974	1.107 (C-H propane) 1.117 (C-H butane)	\$67.47	083190
dnosO		1,60061	1.03299	12660,1	1,09 (rttp/1 chloride)	1,22265	0.64537
(-H (CH1)	(i) Group	1.64010	1.04566	1.10668	1.10 Consequential (consequential) 1.108 (asp.) (1.3-tentalisme)	1.26354	95/190
droug (iii) ( - (		2.04740	1,43087	1.51437	1.508 (S.1 \$02.1	1,46439	0.6987
C'-('ii) Group		2.04740	1,43087	1,51437	. 1.508 (2-hutene)	1,46439	0.69887
Oraup () :7-()		2.04740	1,43087	1.51437		1.46439	0.69887
C≠C Group		1.47228	15997:1	1.34052	1.342 (2- mathylocyans) 1.346 (2-huma) 1.349 (1.3-husadizze)	0.75055	0.86030
D-0	d	2,19358	1,64243	1,73827	1,730 (viny chloride) 1,73 (1,1- debloredridee	1,45403	0 74874
C-C()		2.15818	1.62912	1.72419	1.730 (vinyl chloride) 1.73 (1,1- dichlorochylene	1.41552	0.75486
Parameter		0 (0,)	0, (0,)	Bond Length 2c' (A)	Exp. Bond Length (A)	6,0 (0,)	,

1804 15.55. The MO to HO intercept geametrical bond parameters of branched-chain alkery chlondes. If R.R. are H or alky typoux. E, is E, atom - atom, may AO.	eincal bon	d parameters of	branched-chain p	dkenyi chlonde:	H, R', R" are	H or alkyi grou	103. E, is E,	atom -atom, n	nw. 40).						
	F F F	Δt ;	٠. د د	F.F.	.d	Final Total	j	į	() ()	E(C2491)	6	65	σ.	9	1,0
		Bond 1	Bond 2	(cv) Bond 3	Bond 4		(°)	(a,	Find (eV)	Final	€_	€	€	હ	ું
$C_{\bullet} = C_{\bullet}(CI) - H_{\bullet}(CH_{\bullet})(I)$	Ju.	3.245.I.	22,57	e	c	30HLF 851-	0.91771	0.81549	-16.68412	-16.49325	76.99	10,7,01	40.53	1,21633	O IEUS
-C'=C'(H)C1 (C'-C1 (0)	ن	07.EL.J.	פענה	æ	e	201/LF EST-	4,91771	GASIAG	-16 68412	-16.40335	79 43	72,004	74.69	1.71672	0.1498
-C'=C'(H)Cl	દ	ניונטי	c	·	a		1.05158	0.87475	.15.55033		A5.36	75.8	38.03	1.69995	0.0708
(C, -cr (ii)) -c, = c, (C)(r)	Ų.	1.133779	-0.46439	#IGZG·U*	è	154 (4326	111160	a.784INS	5K85.71-	-17,16245	73.67	107.03	ZO.RE	1,11153	0.2401
וכ"-נו (ש)) -נ"=נ"נטנ <i>ו</i>	23	65 FDFUr	С	-	۰		1.05158	0.R8DN3	-15.39034		83.62	36.38	37.46	(74125	8000
C*(H)C' = C'H'C'	ر:	-1.1330	AI 929 I K	a .		-153 67867	17716.0	19508.0	CT8101 21.	-16 69786	127,61	ects	35.2	0.77492	0.4916
C,(H)C,=C,H,	ť	-1,13140	u	C	e e	-152.74949	0,91771	0.85253	-15.95955	-15.76868	129.84	\$0.76	66.70	0.017.0	0.5462
C,(C,)C, =C,H,C,	Ü	-1.1330	721/21/O-	-0.73457	0	-134.19803	17719.0	0.78155	-17.40809	.17,21783	126.39	1975	56.95	0.80289	0,4637
なられ。一つ。(C) = C (C - C の)	Ċ,	-6.3,73140	13857A	tsrct.o-	a	134 19801	177160	0,78155	-17,40869	-17,21713	8	11811	17.79	1.11127	O.Jento
(C=C (ii)) (C=C (i)) (C=C (ii))	່ ນ	שמנט	-0.9291R	e	. 8	SPEAT IS 1-	17718	1952810	1841-91-	-16,21864	67.10	112.60	31.36	1,74821	4718.0
<i>R</i> (', <i>H</i> , − (',( <i>H</i> ) = (') (C − (' (ii))	U	-4.13390	A) OZ U.O.	С	e	-133 677146	17116.0	0.80561	-16 88873	976991-	64.57	115.63	20.79	1.77684	0.34590
R(C,H,-C,(H)=C (C-C (i))	ຳ	-0.929IR	-0.9391R	٥	c	-133.47.05	17716.0	O.R1549	-16 69411	.16,49323	65.59	1140)	30.58	L.XG270	631KG
$C - H (CH_1) (t)$	Ü	-1.17190	=	c	e	-152.74040	0.91771	0.63252	-15.05955	-15.76868	77.13	102.85	44.13	1,23531	0.18965
C-H (CH,)	Ü	49,92918	ı	u	٥	-152.54487	17719.0	0,86359	-15.75473	13,56407	77.49	102.51	41.45	LZISCA	Q. ISTOR
$(-H(CH_1)G)$	J	-0.9291#	AIUSSIIK	0	e	-153.47400	177190	0.81549	-16 GM[2	.16,49525	C# #55	111.53	35.64	1,35486	0.29933
C-H (CH) (II)	ij	HIGZGU*	#ICC.O.	-0.92918	e	-154,40334	0.91771	0.77347	0551971-	.1741344	61.10	118.30	TC.IE	1.47989	2073
H,C,C,H,CH, (C'-C'(8))	نن	81626.0-	c	c	0	-152.544R7	0.91771	0.86339	-13.75493	-13.56407	63.82	116.18	30.08	1.83879	0.33106
H,C,C,H,CH, (C('(a))	۲,	A19201A	* C\$6.0-	c	e.	-153 47406	1,51,771	675 IX'U	-16,68413	-16.49325	19:95	13.59	9072	1.00830	0.45117
R-H,C,C,(H,C,-10)HCH,- (C-C,0))	ť.	-0.0291R	NIGEGO-	\$1626'U*	5	-191,40ga	177160	a77247	-17,61330	17.42344	6,30	131.70	31.80	1,57162	0.51388
$R = H_1C_1(R - H_1C_2)C_4(R^2 - H_1C_2)CH_1 - (C - C_1C_2)$	ر.'	я1626'0-	13121.00	72X7.0-	-0.72457	-154.71860	0.91771	0.73889	-17.92500	917.77.	48.21	51.73	7.72	H282.1	0.505.0
Ital', C', (H, C', - II') HCH, - (C'-C' (d))	ن	41991x	N162GO	4,92918	e e	-154.40334	R.91771	111110	-17.61330	17.42244	48.30	07,161	21.30	1,97162	0.51388
(C-('(e))	ڻ:	-4 72457	72,457	4.7357	- 72M57 a	66815.1811·	11116.0	0,7676.5	-17.523Kh	פתנו,לו.	वद	129.96	22.00	134467	Z62670
$ienC_{\mathcal{L}_{i}}(H_{i}C_{i}-R^{i})HCH_{i}-$ $(C-C_{i}(0))$	ئ	75157 0.	ијесе о-	#16 <u>7</u> 6 tr	ď	-154.19863	0,91771	0.72155	-17,408(0)	-17.21783	52.7%	27.0	200	1,9241	0 47,779
$imC_s(R'-H_sC_s)C_s(R'-H_sC_s)CH_1-IC_s(C)$	٠٠	12157	121.57	4,71157	12LT.O.	.154.51399	17716.0	0,76765	-17.92866	977.71-	800	129.26	32.00	1.94462	0.49298

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် ခြ	je	C=C Group	() -(; () Gaup	(ii)	(iii) Group	Group	Group	goog	C. (ii)	Group Group	(E) day	(a) - (c) (d) (d) (d) (d) (d) (d) (d) (d) (d) (d	Group	Group	C-C (e)	Group
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0	•	•	•	•	•	-	0	1	-	0	0	٥	0	0	0	٥
-	0	•				•	•	•	0	•	0	٥	0	0	0	0
0.5	29	23	29	20	. 50	0.75	0.75	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
0.81317	0,81317	171160	-	-	-	-	_	-	1	-	1	_	-	1	-	-
-	-	-	_	-	-	-	-	-	-	-	-	-	-	1	1	1
-	-	171160	17716.0	0,91771	17710.0	17716.0	17716.0	17716.0	0.91771	17716.0	17716.0	17716.0	0.91771	17716.0	0.91771	17719,0
-	0	0	_		-	-	-	•	-	-	0	0	0	-	-	0
7	~	4	7	7	~	-	_		-	-	2	7	2	2	2	2
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20	0.5	0.5	0.5	20	.50	0.75	0.75	0.75	0.75	0.75	0.5	0.5	50	0.5	0.5	50
0,81317	0.81317	17716.0	-	-	-	-	-	-	1	-	-	1	-	-	-	-
.3287721		-102,08992	-30,19634	-30,19634	-30.19634	-72,03287	-37,10024	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.101.12	-28.79214	-29.10112	-29.10112
8.35160	8.28304	21.48386	9.50874	9.50874	9.50874	26.02344	13.17125	38.02728	25.78002	12.87610	9.33352	933352	6.37273	9,33352	9,37273	6,372,73
7,61688	7,32700	34.67062	7,37432	7,37432	7,37432	21.95990	11.58941	32.53914	21.06675	10.48582	6.77464	6,77464	90500	6,77464	6.90500	6,90500
-3.80844	-3.66350	-17,33531	-3 687 10	-3.68716	-3.68716	-10.97995	-5.79470	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3,38732	-3.45250	-3.45350
-14,63489	-14.63489	0	-14,63489	-14.63489	-14.63489	-14,63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15,55407	-15,35946	-15.56407	-1535946	-15.35946
-3.71674	-3.19677	٥	٥	q	0	0	-1.13379	0	0	0	0	0 .	0	С	٥	۰
-10.91815	-10.97139	0	-14,63489	-14,63489	-14.63489	-14,63489	-13,50110	-15,56407	-15.56407	-14.63489	-15.56407	.15,56407	-15,35946	-15.35407	-1535946	-15,35946
31.63531	-31,63541	-63.27075	-31.63534	-31.63534	-31.63534	49.66437	-31.63539	-67,69451	49,66493	-31.63533	-31.63537	-31.63537	-37.63535	-31.63537	-31.63535	-31,63535
-1,44015	-0.92918	-2.26759	-1,44915	-1.85836	-1.44915	0	0	0	0	0	-1.85836	-1.85836	-1,44915	-1.85836	-1,44915	-1,44915
-33,08452	-32.56455	-65.53833	-33,08452	-33,49373	-33 08452	49.66493	-31.63537	-67,69450	-49.66493	-31.63537	-33.49373	-33,49373	-33,08452	-33.49373	-33.08452	-33.08452
8.31434	8.11389	43,0680	0,07851	16,4962	9,97851	25.2077	26.4826	24,9256	24.2751	24.1759	. 9.43699	9.43699	15,4346	9,43699	9.55643	9.55643
5.47264	5.34070	28,34813	6.56803	10,85807	6.56803	16.59214	17.43132	16.40846	15.97831	15.91299	621159	6,21159	10,19220	6,21159	6.29021	6.29021
-0.15312	-0.14888	-0.34517	-0.16774	-0.21834	-0.16774	-0.25493	-0.26130	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
0.08059	0.08059	0.17897	0.15895	0.09931	16990.0	0.35332 Eq. (13.458)	0.3532 Eq. (13,458)	0,3532 Eq. (13,458)	0,35532 Eq. (13,458)	0.35532 Eq. (13.458)	0.12312 [2]	0.17978 [4]	0.09944	0,12312 [2]	0.12312 [2]	0.12312
-0.11282	-0.10859	-0.15568	-0.08827	-0.16869	-0.11809	-0.07727	-0.08364	72727.0-	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803	0,14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803
-33.19734	-32.67314	-66.04969	-33.17279	-33,66242	-33.20260	-49.81948	.31,71901	-67,92207	-49.80996	-31,70737	-33.59732	-33.49373	-33,24376	-33.59732	-33.18712	-33.18712
-14,63489	-14.63489	-14,63489	-14,63489	-14,63489	-14.63419	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63419	-14,63489	-14,63489	-14,63489	.14,63489
0	0	0	0	0	0	-13.59844	-13.59844	-13.59844	-13.59844	-13.59844	0	۰	٥	•	۰	٥
3.77953	3,40336	7,51014	3.75498	4,39264	3.78480	7.83968	3,33765	12,49186	7,83016	3.32601	4.32754	4,29921	3.97398	4,17951	3.62128	3.91734
	<del>▗▗▗</del> ▗▗▗▗▗▗▗▗▗▗▗▗▗▗▗▗▗▗▗▗▗▗▗▗▗▗▗▗▗▗▄▗▄▗▄▗▄▗▗▗▗	(ii)  (i)  (i)  (i)  (i)  (i)  (i)  (i)	(ii)  Circupt  1  0  0  0.5  0.51317  1  1  1  1  0.051317  -32.1474  -32.1474  -32.1477	(ii) G = C = C   G   G   G   G   G   G   G   G   G	(ii)   G=C   G=0   G=0     1	Group   Grou	(ii) Gae2 (-iv) (-	(ii)   Grach   Grach	(ii)   Ge=C   Geap   Group   Group	(ii)         G=C         Gach         Gach	(ii)         G=C         Gach         Gach	Chargo   C	(i)         Graph         G	(1)11/10         C cont         C con	Quinty         Genety         Cristy         Group         Group	(1)         (2 = 2.4.1)         (2 = 0.1.1)         (

၂၂ ن ن-ن . . 

	(e) (e)		124 (ringi chlaride)	(12.5 (Nith) thisolde) 12.8 (1.1-dichlumahrkane)	(1,1-Suhkorodáybne) (12,5 (12,5 (12,6) (13,1)			13.4 decades (1.3.3 decades (1.3.3 decades (1.3.3 decades (1.3.4 d		118,3 (2-neth) (perpent)	(2-methylyrepene)	107 (propane)	12 (prop.ac.)     13 8   10 8   10 8 (perbutano)	(111.0 (Patane) 111.4 (Isobiates)				110.8 (sechnitane)		(isokume)	111.4 (behtane)	
		15.2	121.59	131.53	81 ED	118.36	113.84	97 KI	118.19	11631	121.85	108 41	110.49	110.49	309.50	105,44	100.44	110.67	110.76	6311	11.27	3,701
. 1	e, ©								13.46													
, utu.	e. C		11694	116,94					18.36		116.31											П
m - aka	ø, ©												15.69	1569		70.56	70.56					82.7
ed. C, is E, (all	(eV)	0			н 16 <u>2</u> 0-0-	e	-1.8936	928811-		U		0		.•	c			+1.85R.W	0	0	+1.85836	
igle were us	v	1,00773			0 אפנצט	ושפיז	ดรางก	5001310		0.17300		1,13796			1.15796			07180	18890'1	1.04887	1,04887	
ceding as	υ <u>-</u>	0.75			-	0.75				87 U		0.75			Q.75			1	0.75	n.15	a.75	
ron the pre	<del>ن</del> '	0,95310 (Est (15 65))			0,81317 (15.13)	-	-	-		-		-			-			1	•	-	1	
anmeters fi	υ U	a.75			-	6.75	-	-		-		-			-			1	a.75	87.0	0.75	
of B. the p	5 E	0.91771		•	0.86359	0.91771	0.815.19	0.815.49		-		-			-			กุลเรเข	0.91771	กรเกา	0.91771	ŀ
calculation	4 J	0 83,600			0 26359	0 15251	041549	0 13561		\$525×0		O.MCUSD			OSLUMO			0.81549	CG+LA ()	SGLTKU	0.87495	
values [1]. In the	Hybridization Diseparties	В			5	1	a	**		=	-	11	-		=			×	-	1	-	
xperimental	Acres 2	-12.96764 C.1			12.90764 (3)	.ts 10,575	-16 64411 C,	المهاد ب		=		Ξ			Ŧ			Citayuji-	-14.81575 C.	.14 R2573	-14,10,575	
y chlorides and o	Alien I Hebridization Designation (Table 18.3 A)	51			-	r	a			ь		,			٠			22	ş	3	\$	
d-chain alte	Į.	.(6,3743) (°,			*) (0515)-	, C., L.	'.) เเษยม-	-اد بعادی		-15.95935		15.75193			1575493			יועפאיוז.	.15.5303 C.	-1533033 C.	.(13.5503) C.	
branche	(e)	4.541)			\$ 174.0	2765	4201 F	4.7539		371750		34253			3.4252			4,7958	4,1633	4.1633	4.7938	
melers o	, <u>, , , , , , , , , , , , , , , , , , </u>	3.256.5			1362	236175	2346175	2.Mel73 4.73.39	Г	304578		211106			10701	П		291347	2.11733	1,007	120012	
dangle para	, <u>, , , , , , , , , , , , , , , , , , </u>	JAC SIK			15052	21133	\$CIVAT	153321		2r457K		2.11106			2.09711			1418.5	ואוננ	1.91547	2,90327	
Table 15.55. The bond angle parameters of branched-chain alternyl chlorides and experimental values [1]. In the catoliation of B., the parameters from the preceding angle were used. E. is E, fatom - anony arty. AO]		(0, -0.1	(C, -(7, (i))	(C, = C, C)	(() -(.) (() -(.) ())	(c;(H)c;=c;)	('\'='\')('\') '\'\'\'\'	('5'5='5) '5'3'7	לאני, כי	(H,C,=C,C,)	('.'' = '.''(.') (''' - ''' - '''	H. H.	שניטיני	H'5'.37	H, 7H2		H,7,72	בנ"נ"נ' כנ"נ"נ'	Δ',C,H C,	π'ς'.π ''	יייי כ', ערינ'נ'	'C'C'C'

ALCOHOLS 
$$(C_n H_{2n+2} O_m, n=1,2,3,4,5...\infty)$$

The alkyl alcohols,  $C_n H_{2n+2} O_m$ , comprise an OH functional group and two types of C-O functional groups, one for methyl alcohol and the other for general alkyl alcohols. The alkyl portion of the alkyl alcohol may comprise at least two terminal methyl groups  $(CH_3)$  at 5 each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the 10 isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alcohols are equivalent to those in branched-chain alkanes.

The *OH* functional group was solved in the Hydroxyl Radical (*OH*) section. Each C-O group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$ . 15 shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the O AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl alcohols, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)) and the O AO has an energy of  $E(O) = -13.61806 \, eV$ . To meet the equipotential condition of the union of the C-O  $H_2$ -20 type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the

$$c_2\left(C2sp^3HO\ to\ O\right) = \frac{E\left(O\right)}{E\left(C,2sp^3\right)}c_2\left(C2sp^3HO\right) = \frac{-13.61806\ eV}{-14.63489\ eV}\left(0.91771\right) = 0.85395 \quad (15.114)$$

C - O-bond MO given by Eqs. (15.68) and (15.70) is

 $E_T(atom-atom, msp^3.AO)$  of the C-O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is  $-1.65376\,eV$  for the  $CH_3-OH$  C-O group. It is based on the energy match between the OH group and the  $C2sp^3$  HO of a methyl group and is given by the linear combination of  $-0.92918\,eV$  (Eq. (14.513)) and  $-0.72457\,eV$  (Eq. (14.151)), respectively. For the alkyl C-O group,  $E_T(atom-atom, msp^3.AO)$  is  $-1.85836\,eV$ . It is based on the energy match between the O AO and the  $C2sp^3$  HO of a methylene group where both energy contributions are given by Eq. (14.513).

The symbols of the functional groups of branched-chain alkyl alcohols are given in Table 15.57. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl alcohols are given in Tables 15.58, 15.59, and 15.60, respectively. The total energy of each alkyl alcohol given in Table 15.61 was calculated as the sum over the integer multiple of each  $E_D(Gmup)$  of Table 15.60 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl alcohols determined using Eqs. (15.79-15.108) are given in Table 15.62.

$C-H(CH_1)$	<i>H</i>	-(; (a)	-(c)	(9)	(g) )-	-(. (e)	ر-ر. (۱)
CH, group ('-							CC (1 to iso-C)

17.47.	2000	2000		2:2:2:								
1.52750	1.52750	1.54616	1.52750	1.54616	1.54616	1.29924	1.29569	1.27295	1.18107	1.19429	0.86925	h,c (a,)
(butane)	(butane)	(butane)	(butane)	(butane)	(butane)		(C-H butane)	(C-H butane)			(methanol)	
1.531	1.531	1.531	1.531	1531	1.531	(isobutane)	1.117			(methanol)	0.9451	3
(propane)	(propane)	(propane)	(propane)	(propane)	(propane)	1.122	(C - H propane)	(C-H propane)	1.431	1.4246	(ethanol)	Cengili
1532	1.532	1.532	1.532	1.532	1.532		1.107	1.107			0.971	Exp. Bond
1.53635	1.53635	1.54280	1.53635	1.54280	1.54280	1.11827	1,11713	1.10974	1.41303	1.41785	0.971651	bond Length 2c' (A)
1.45164	1,45164	1.45744	1,45164	1.45744	1.45744	1.05661	1.05553	1.04856	1,33512	1.33968	0.91808	c' (u,)
2.10725	2.10725	2.12499	2.10725	2.12499	2.12499	1.67465		1.64920	1.78255	1,79473	1,26430	0 (0,0)
Graup	Group	Group	Group	Group	Granb	Group	Group	Group	Group	Group	Group	
(J) 2-2	(e) C-C (e)	(p) 2-2	(6)	C-C (b)	(a) ひひ	C-#		$C-H(CH_c)$	(ii)	(E)	₹,	Parameter

the state of the s			414 y . a. c. c. c. c.		or may be outs.	12 13 Er O	.m = aram,msp.								
Bond	Atom	E,	Ē	E,	.83	Final Total			E	11-60/3	,a		,		
		(c V)	<u>ر</u> گ	(§	S	Energy	<u>}</u>	2	5	( c(casp )	. 3	s- 3	<b>5</b>	6-(	, re
		Bond 1	Bond 2	Bond 3	Bond 4	(24)	6	6	Final	Final (	<u> </u>	<u> </u>	E 	(°)	(°
Н-ОЭ,Н	0	-0.82688		e	o	(2)	1 00000	10000	15 65757						
-H <sub>2</sub> C,0-H	0	-0 92918					1 00000	0.0020	1070001-		115.49	64.51	64.51	0.54405	0.37403
н,с-он							2000	0.80339	-13,73493		115.09	. 64.91	64.12	0.55182	0,36625
(C - 0 (i))	-	23078:0-	B	0		-152,44257	17716.0	0.86723	-15.63263	-13,46177	96.39	19'68	46.30	1.23986	0.09381
(C-0(0)	0	0.82688	. 0	0.	•		1.0000	0.86923	-15.65263		65.96	83.41	46.30	1.23926	0.09981
-4,5, -0H {C-0 (ii)	υ,	81626'0-	-0.92918	0.	0	-1 53.47405	0.91771	0.11549	-16,68411	-16.49323	93.09	86.91	43.39	1.29114	0.04393
- <i>H</i> , <b>C,</b> - <i>OH</i> (C <i>O</i> (ii))	0	-0.92918	0	۰	٥		1.00000	0.86159	-15.75493		97.20	82.80	46.50	1 22692	0 10\$20
C-H (CH,)	ن	-0.92918	•	0	0	-152.54487	0.91771	0.86359	.13.73493	-13.36407	27.60	102 51	07.17	1 3166	
C-H (CH;)	υ	40.92918	-0.92918		0	-153.47405	0.91771	0.81549	-16.68412	-16 49325	27 89	63 111	2,5	1.239	0.18708
C-H (CH)	Ü	-0.92918	\$1626.0-	-0.92918	٥	-154.40324	177160	177.00	OFFIA TI	17 43344	5.5		13.04	1,39460	0.29933
H <sub>3</sub> C,C,H <sub>3</sub> CH <sub>2</sub> (C,-C (0))	٦,	-0.92918	٥	•.	o	-152.54487	0.91771	0.86359	-13.73493	-13.36407	21.12	06.911	10.00	1.42988	0.37326
H,C,C,H,CH, -	Ú	81020 0	91869 9	•										118.00	Bien
(('-('(a))				-		-153,47406	0.91771	0.81549	-16.684(2	-16,49325	35.41	65.121	26.06	1.90890	0.45117
$(C - C, \{b\})$	ť	-0.92918	-0.92918	-0.92918	•	-154.40324	17116.0	0.77247	.17.61330	-17.42244	4830	131.70	21.90	1.97162	0.51388
$R - H_2C_a(R^2 - H_2C_a)C_a(R^2 - H_2C_a)CH_2 - (C - C_1 c_2)$	౮	-0.92918	-0 72457	-0.72457	-0.72457	-154.71860	17710	0.75889	-17.92866	67.67.71-	48.21	131.79	21.74	P57724	0.50570
$km',C,(H,C,-R)HCH_1-(C-C,G)$	౮	-0.92918	81626.0-	-0,91918	•	154,40324	177100	0.77247	-17,61330	-17.42244	4830	131.70	21.30	1,97162	0.51388
teric, $(R-H_2C_2)C_3(R''-H_2C_2)CH_3-(C-C,C)$	ď	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	17716.0	0.76765	-17.92866	-17.73779	\$0.04	129.96	22.66	1.94462	0.49298
$lem(C,C,(H_2C,-R')HCH_2-(C-C,O))$	۲,	-0.72457	-0.92918	-0.92918	٥	-154.19863	17716.0	0.78155	-17,40269	-17,21783	52.78	12,22	20.22	1.92443	0.47279
INDC. (R-H,C.)C. (R-H,C.)CH.	ป์	-0.72457	-0.72457	.0.72AS7	-0.72457	-154.51399	17716.0	0,76763	-17.92866	0771771	2 5	20 00	ì		

e 15.59. The MO to HO intercept geometrical bond parameters of alkyl alcohols. R.R.R. are H or alkyl groups. E is E (atom - arom men) 40)

Table 15.60. The energy parameters (eV) of functional groups of	rs (eV) of function	nal groups of alkyl	alkyl afcohols.									
Parameters	HO	() C-0	(i) C-0	ć'H',	CH,	C-H Group	C-C (a)	ر: - ر (a) زناسته	(;-C (e)	C-C(d)	(e) (J-)	ر- ( <del>)</del>
		450		Granp	dnoo							,
n,	-	-	1	3	2	_	-	-	-	-	-	-
<i>'u'</i>	0	0	0	7	1	0	0	0	0	0	0	0
· 0	0	0	0	0	0	0	0	0	0	0	0	0
<u></u>	0.75	0.5	0.5	52:0	0.75	0,75	5.0	5.0	6.0	6.5	6.0	5.0
, i	_	-	-	-	-	-	_	_	-	-	-	-
2	27.0	-	-	1.	-	-	-	-	_	-	-	-
5	_	0.85395	0.85395	17716.0	17719.0	0.91771	17716.0	17716.0	17216.0	0.91771	17716.0	17716.0
ઈ	-	0	0	0	-	-	0	0	0	1	-	0
<i>c</i> ,	1	2	5	1	1	1	2	7	7	2	2	2
, j	-	0	0	ç	2	-	0	0	0	0	0	0
, t	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
	_	1	-	1	1	-	-			-	-	-
V, (cV)	40.92709	-33.47304	-33.78820	-107,32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	14.81988	10.15605	10.19068	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9,33352	9.37273	9.37273
7 (cV)	16.18567	9.32537	9.47749	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V, (aV)	-8.09284	4.66268	-4.73874	-1626957	-10.53337	-5.24291	-3,38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
15(us 10) (eV)	-13.6181	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15,56407	-15.56407	-15.35946	-15,56407	-15.35946	-15.35946
Digusta (m m) (W)	0	-1.65376	-1,85836	0	0	0	0	D	0	٥	0	0
12 (40 m) (eV)	-13.6181	-12.981(3	-12.77653	-15.56407	-15.56407	-14.63489	-15,56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
fr (n.10) (aV)	-31.63247	-31.63544	-31.63529	1569'29-	-49.66493	-31,63533	-31.63537	-31.63537	-31,63535	-31.63537	-31.63535	-31.63535
$E_T(alom - alom, mxp), AO)$ (cV)	0	-1.65376	-1.85836	0	0	0	-1,85836	-1.85836	-1,44915	-1.85836	-1.44915	-1.44915
Er (4m) (cV)	-31.63537	-33.28912	-33.49373	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω (1013 rad 1.8)	44.1776	22.3978	12,2831	24.9286	24.2751	24.1759	9.43699	9.43699	15.4845	9.43699	9.55643	9.55643
$E_{k}$ (oV)	29.07844	14.74264	8.08494	16,40846	15.97831	15.91299	621129	6.21159	10.19220	6.21159	6.29021	6.29021
Fn (cV)	-0.33749	-0.25287	-0.18841	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
E. (eV)	0,46311	0.12808	0.13328 [20]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944 (51	0.12312 [2]	0.12312	0.12312 [2]
$\vec{E}_{ac}$ (aV)	-0.10594	-0.18883	-0.12177	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{n\pi}$ (eV)	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Erleann) (UV)	-31.74130	-33.47795	-33.61550	-67.92207	49.80996	-31.70737	-33.59732	-33,49373	-33.24376	-33.59732	-33.18712	-33.18712
Emayle, so my (cV)	-13.6181	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489
E (c. 10 10) (cV)	-13.59844	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
15,10-r) (aV)	4.41035	4.20817	4.34572	12,49186 ·	7.83016	3,32601	4.32754	4,29921	3.97398	4.1795]	3.62128	3.91734

	Relative	Ĕ	260	9900	1046	0.00098	920	. 100	090	3048	110	620	087	800	7007	1092	174	021	052	16	900	332	010	707	Ę
		_																							
	<u>اس</u> .			33.428	45.584	45.766	57.736	57.922	57.828	58.126	69.887	70.057	70.097	69.957	69.950	70.246	70.083	82,054	82,236	94214	106.358	106.459	118,521	130.676	154,984
	Calculated	Energy (eV)	21.11038	33.40563	45.56333	45.72088	57.72103	57.87858	57.79359	58.15359	69.87873	70.03628	70.03628	69.95129	69.95129	70,311,29	69.96081	82.03643	82.19398	94.19413	106.35183	106.42439	118.50953	130.66723	154.98263
	ر-د (۱)		<b>o</b>	0	c	0	0	0	0	0	0	0	0	0	0	0	٥.	0	0	0	0	0	0	0	0
	(a) 2-2		0	0	0	<b>.</b>	= 0	<b>5</b> (	0	ь.	0 (	e (	۰ د	0	0	0 (	0 (	0 1	0	0	0	0 1	۰ د	۰ د	0
	(d)	,	<b>5</b> (	<b>5</b> (	c (	<b>o</b> 6	<b>.</b> .	> <	> 0	<b>-</b> •	<b>5</b> 6	> 0	> 0	۰ د	-	۰ د	- «		۰ د	<b>.</b>	۰ د	٥ ،	> 0	> 0	0 (
ional group composition and the energies of Table 15.60 compared to the experimental values [3]	(c) (c)		> <	> 0	- -		> 0	•	> 1	n c	> <	> 0	> <	> <	> -	n c	> <	> <	-		- (		> <	> <	> 0
to the experime	(a) U-U			•	<b>.</b>	s c	• •			> <	•	· c	· "	۰ ۳	n c	<b>-</b>		• •	> <	> <	> ~	n <b>c</b>	•		> <
.60 compared	(a)	c	, -	٠,	4 C	a er		c		. 4	. 4	. 4		۰ -		. с	. ~			, ,		rec	. 0	.=	<u></u>
ics of Table 15	5	0				0	_	-	0		_	_	-	_	0	7	0		. c		. –	. 0	0		
and the energ	· ·	0	_	7	0	m	_	_	0	4	7	7	2	7	-	0	5	•	9	1	13	· 00	6	=	. <u>v</u>
ip composition	<b>.</b>	-	_		77	_	7	7	m	_	~1	~1	C†	~	۳.	٣.	_	7		_	7	-	÷	_	_
functional gro	Group	-	-	_	_	_	-	_	_	_	-	_	_	_	_	_	-	-	_	_	_	_	-	_	_
lated using the		0	0	0	0	0	0	0	0	c ·	0	0	0	0	c	0	0	0	0	0	0	0	0	0	0
alcohols calcu	Group	-	_	_	_		<b>-</b>								_			_	_	_				_	-
ergies of alkyl								ioner.	nano.			•	ious.	lon.	lon.	nog.					0				
he total bond en		Methanol	Cinanol	ropanol	2-Propanol	-billianol	Andrei C	-Interniting - I-propagation	Princuly:-2-propanano	Pentanol	-renianoj	-renianoi	- Wednyl - I - Oxidenano	-ivicuityi-1-ourananoi	Welliyi-2-Diffananol	- Medinyl-2-butananol	L'accessor	cxanoi	- neplanoi	Ccianoi	- Elhyl-I-hexznanol	-Nonzhol	Dedament	Onecalion	-Hexadecanol
Table 15.61. The total bond crespies of alkyl alcohols calculated using the function remuta $\frac{OH}{C-O}$ (i) $\frac{C-O}{C-O}$			_				•		٠.		•	• •	•	, ,		٦-	- •	•		- (	٠, ٠			•	7

E	101.53	(methanol)	103 (ethanol)	107.8 (ethanol)	(propare)	(propere) 13.8 (butane) 110.8 (sobutane)	111.0 (butane) 111.4 (isobutane)				(rsobutane)		111.4 (isoburane)	111.4 (isobutane)	
<u>3</u> :©		Ş	106.78	110.17	108.44	110.49	110.49	05.601	109.44	109,44	110.67	110.76	111.27	11.27	Ī
ø, ©	_					69.51	169.51		70.56	70.56					-
E,		•	0	-1,65376	0			•			-1.85836	٥		-1.85836	
`v"	i		127.19.0	0.\$3472	1,15796			1.15796			0.81549	1.04687	1.04887	1.04887	
ď		3	6.75	-	0.75			0.75			1	57.0	\$T.0	0.75	
ຜັ		-		-	-			-			1	-	1	ı	
ᢆ		3	0.75	1	1			-			1	67.0	51.0	82.0	
C <sub>1</sub>	11100	1116	177.16.0	0.85395 (Eq (15.114))	ı			-			0.81549	12216'0	17716.0	17716.0	
C <sub>1</sub>		•	1	0,81549	0 86359			0.86359			0.81549	0.87495	0.87495	0.87495	
Atom 2 Hybridization Designation	(Table 15.3.A)	•	1	o	н			æ			25	-	-	-	
Eronade Atom 1			-14.82575	90819 (1-	Ħ	·		Ξ			-16.68412 C.	-14.83575 C.	-14.82575 C,	-14.82575 C.	
Atom 1 Hybridization Designation	(Table 15.3,A)	-	-	×	7						££	s	\$	s	
E-mark			-14,82575	-16 68412	-15.75493			-15.75493			-16.68412 (',	°.)	-15,55033 C7	-15 55033 (',	
2c' Terminal Aleas ( a <sub>a</sub> )	2000	3.003	3,6515	4.5826	3.4252			3.4252			4 7958	4 1633	4 1633	4 7958	
2c° 1pm13 ( a, )		9	1.83616	2.67024	2.11106			2 09711			2.91547	211323	1.00711	2.903.27	
2¢° Donal I (a <sub>a</sub> )	,	40(4)3	2.67024	291547	2,11106			2.09711			2,91547	2.91547	191547	72809.2	
Alums of Angle	Н0.∵Э	(C, -0 (I))	((i) O-'.)) HO'.)7	(C, -0 (ii)	Mohrhma ZHC; H	ענ'ניצ'.	H'.Ś.)7	Mede 1	7,5,5,77	H*.5".77	<b>∠</b> α;ς;ς, ⊷.ς;	H".);77	H,2,72	ישונ" ענ"נ"נ"	

ETHERS  $(C_n H_{2n+2} O_n, n = 2,3,4,5...\infty)$ 

The alkyl ethers,  $C_n H_{2n+2} O_m$ , comprise two types of C-O functional groups, one for methyl or t-butyl groups corresponding to the C and the other for general alkyl groups. The alkyl portion of the alkyl ether may comprise at least two terminal methyl groups  $(CH_3)$  at each 5 end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the 10 isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in ethers are equivalent to those in branched-chain alkanes.

Each C-O group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO 15 and the O AO to form a MO permits each participating orbital to decrease in radius and energy. In alkyl ethers, the C2sp3 HO has a hybridization factor of 0.91771 (Eq. (13.430)) and an energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)) and the O AO has an energy of  $E(O) = -13.61806 \, eV$ . To meet the equipotential condition of the union of the C - O  $H_2$ type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_1$  of Eq. (15.52) for the 20 C-O-bond MO given by Eq. (15.113) is  $c_2(C2sp^3HO \text{ to } O) = 0.85395$ .  $E_r(atom-atom, msp^3.AO)$  of the C-O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is  $-1.44915 \, eV$  for the  $CH_3 - O -$  and  $(CH_3)_3 C - O -$ C-O groups. It is based on the energy match between the O AO, initially at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively), and the  $C2sp^3$ 25 HO of a methyl group as given by Eq. (14.151). For the alkyl C-O group,  $E_r(atom-atom, msp^3.AO)$  is -1.65376 eV. It is based on the energy match between the O AO and the  $C2sp^3$  HO of a methylene group and is given by the linear combination of  $-0.72457 \, eV$  (Eq. (14.151)) and  $-0.92918 \, eV$  (Eq. (14.513)), respectively.

The symbols of the functional groups of branched-chain alkyl ethers are given in Table 15.63. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl ethers are given in Tables 15.64, 15.65, and 15.66, respectively. The total energy of each alkyl ether given in Table 15.67 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.66 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl ethers determined using Eqs. (15.79-15.108) are given in Table 15.68.

								•							
25 of alkyl ethers.	Group Symbol		(i) 0-2	C-0 (ii)	( 10) H = 0	(6,75) :: >	(HU) H-U	(",,,) ;; ,	H-2	C ~ C (a)	C-C (b)	(a) U-U	C-C (d)	(3) (1)	(a) 0 - 0
Entrange of allowing of tunctional groups of alkyl others.	runctional Group	C-O (CH, -O - and (CH,), C -O -)	C-O (allw)	( ( ( ( ( ( ( ( ( ( ( ( ( ( ( ( ( ( (	CH, group	5	dnorf tun	СН	CC bond (n-C)	CC bond (iso.C)	CC bond (true, C)	CC disp to isp.			CC (tto iso-C)

	,	ر د د	Group		2.1072		1.4516		1.5363			1.532	(propane	1.531	(Butane)			
		2 1 2	dnes		2.10725		1.45164		1.53635			1.532	(propane)	1.531	(butane)		1 50750	
	C-C (d)	Grana	dio.	100,01	2.12499	1 45711	1.43/44		1.54280		-	7601	(propane)	157	(outane)		1.54616	
	(a) U-U	Group	-	2 10725	2.10123	1.45164		1 63636	20000		1 533	(annua)	1 531	Chittana	(ontains)	1,000	05/751	
	(e)	Group		2.12499		1.45744		1.54280			1.532	(propane)	1.531	(butane)		1 54616	200000	
(6) (7-7)		d'anno		2,12499		1.45744		1.54280			1.532	(propane)	1.531	(butane)		1.54616		
C-H	Group		1,69467	1.07403	1 06661	1,00001		1.11827				1.122	(sopporane)			1.29924	2000	•
$C-H(CH_{\bullet})$		Croup	1,67122		1.05553			1.11713		1.107	H~2)	propane)	1.117	(C-H butane)	1 70550	1.47.307	0,63150	77.00
$C-H(CH_{\bullet})$	20.00	CIONE	1.64920		1.04856			1.10974		1.107			•	(c - r butane)	1.27295		0.63580	
Group	dago	221.02	1.794/3	2,000	1.33968		141785	Car It.		•	1.418	(cthy! methy! ether (avg.))			1.19429	0.74645	0.000	
Group		1.80717		1 34411			1.42276			1416	Oltri olimpiani oli	(content) ciner)		37705 1	0//07::	0.74388		
		(°°)		(a)		T Tolling	Leanger .	1c. (A)	ם מים	Length		₹ -		b,c (a,)		8		

Table 15.65. The MO to HO intercept geometrical band parameters of alkyl ethers. R.R.R" are H or alkyl groups. Fr is Fr (arom - arom, mrp' MO)	trical bond	parameters of al	kyl ethers. R.R	.R" are Hora	ikyi groups. Fr	is Er (alom -	atom, msp".AO	<u>`</u>							
Bond	Atom	E, (eV)	(eV) Bond 2	E, (eV) Bond 3	(eV) Bond 4	Final Total Energy (C2sp)	[s]	[] (e	Final (eV)	E(C2xp²) (eV) Final	·6 ①	e, ©	θ°.	(°)	(a, 1, 1)
C-H (NC, H,)	ن.'	T2M57	6	9		.152.34026	17716.0	0.87495	.15.55033	11,35946	. 58.11	101.15	42.40	ותובו	0,16921
H,C,-0-C,H, (CH,),C,-0-C,H, (CH,),C,-0-C,(CH,), (C-0 (!))	ئ	-0.72457			0	750±€.£81-	0,91771	0.87495	.15.55033	.13.33946	16:56	14.03	46,10	91622.1	0.09112
H.C., -0-C.H., (CH.), C., -0-C.H., (CH.), C., -0-C., (CH.), (C-0.0))	0	-0.72457	-0,72457		6		1.00000	0.83600	-1627490		72.66	27.78	43.74	1,30555	0.03\$76
$-H_{\zeta_{\alpha}}-\Omega_{\zeta_{\alpha}}(CH_{\beta}),$ $-H_{\zeta_{\alpha}}-\Omega_{\zeta_{\beta}}H_{\beta}$ $(C-O\ (ii))$	u'	-0.82622	-0,9291R		0	53175.531.53	17719	0.12053	-(6.58181	16.35095	92.41	\$7.39	43.55	1,305 (2	0.03456
$-H_iC_i - OC_i(CH_j)_i$ $-H_iC_i - OC_iH_j$ $(C - O(ii))$	O	-0.72457	-0. R2GHB	0	0		1,69000	4,1307£	0,27720		93.33	16.67	43.9K	1,29138	0.04129
$-H_1C_a - O - H_1C_a - (C - O - O - O - O - O - O - O - O - O - $	0	-0.F26EB	-0.R26KK	0	•		1.00000	0.12562	-16,47951		72.87	87.13	43.66	678673	0.04138
C-H (CH,)	ز	.0.92918		-		-152.34487	17410.0	0,16359	-13.75493	-15.56407	77.49	16201	41.48	1,23564	Q.18708
C-H (CH <sub>2</sub> )	U	-0.9291R	-0.9291R	0	٥	-153,47406	17710.0	0,81549	-16.61412	-16,49325	68.47	111.53	35.84	1.35416	0.29733
C-H (CH)	ر	-0.92912	8102010-	-0.92918	0	-154 40324	17710.0	0.77247	-17,61330	-17,42344	61.10	118.90	31.37	1.42988	0.37326
H,C,C,H,CH2	ť	#1619.0-	0	e	•	-152.54417	17710,0	0.86359	-15,75493	-15.56407	63.82	81'911	30.08	1.83879	0.38106
H,C C,H,CH <sub>2</sub> -	ť	-0.92918	#1626'0"	٥	•	-153.47406	17710.0	0,11549	-16.68412	-16.49325	55.41	123.59	26.06	1,90490	045117
$(C - C'(h_1^*C_1 - K')HCH_2 - (C - C'(h))$	υ,	#1626.0·	-0.9291#	\$1929.p-	C	-154 40324	0.91771	0,77247	-17.61330	-17,42344	48,30	131.70	21.90	53176.1	O.SIJNK
$H - H_2C_*(R - H_2C_*)C_*(R^* - H_3C_*)CH_3 - (C - C (e))$	ن:	#1626.D-	-0.72457	15457.0-	4,72457	-154,71860	17716.0	0.75889	-17.92166	017.67.71.	4K.31	131.79	21.74	ber80.1	0.502.0
$lsaC_{s}C_{s}(H_{s}C_{s}-R)HCH_{s}-(C-C_{s}(d))$	ڻ	-0.92918	-6 9291R	-0,92918	0	-154,40324	17710.0	0.77247	-17.61330	-17,42264	48,30	131.70	21.90	20126'1	0.513RR
(C-C'(e))	ر.	-0.72457	-0,72457	-0.12457	-0.72457	-154.51399	1221771	0.76765	-17.92866	-17.73779	\$0.0N	96'621	22.66	29461	0.40298
(C-C, G)	۲,	-0,72457	*10 <u>7</u> 291#	41,9291 K	-0	-(34,19863	17716,0	0.78155	-17.40869	-17.21713	\$2.78	27.731	24.04	1.92443	0.47777
$lim'_{*}(R-H_{i}C_{s})C_{*}(R-H_{i}C_{s})CH_{s}-$	2,	-0.72457	-0,72457	-0.72457	15 P. 77 157	-154.51399	177100	0,767/65	-17.92866	-17,73779	10,02	129.96	22.66	1.94462	0.49208

Description   C-0 (i)   C-0 (ii)	00-5	(1) (1) (1)	CITICIA.	7	H	(B) .))	(q)	()-(;	(P) U-U	(e) U-U	ر-ر (ا
an a	Group	Group	r S	Group	Greup	Oreup	Group	Group	Group	Group	Group
7	-	-	3	2	-	-	-	~		1	-
	•		,	-	o	0	0	0	0	0	0
	,	·	0	0	0	0	0	0		٥	
	20	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0,5	0.5	0.5
	-		-	_	-	-	-	-	-	1	-
	-	-	-	-	-	-	-	-	-	-	-
	0.85395	0.85395	0.91771	0.91771	177160	17716.0	0.91771	0.91771	0.91771	17716.0	17716.0
	0	0	0	-	_	٥	0	0	1	-	0
.5	7	2	_	_	-	1	2	2	2	2	2
	0	°	3	2	-	0	0	0	С	0	٥
	0.5	0.5	0.75	0.75	0.75	0.5	6.5	0.5	6.5	0.5	0.5
	-	-	_	-	-	-	_		1	1	-
P. (cV)	-33.15757	-33.47304	-107,32728	-70,41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.101.12
V, (aV)	10.12103	10,15605	38.92728	25.78002	12,87680	0,33352	9.33352	9.37273	9.33352	9,37273	9.37273
7. (eV.)	9,17389	9.32537	32.53914	21,06675	10,48582	6,77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_ (aV)	-4.58695	4.66268	-16.26957	-10,53337	-5.24291	-3,38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(m m) (aV)	-14.63489	-14.63489	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15.35946
ΔF <sub>U,m</sub> (w w) (eV)	-1.44915	-1.65376	0	. 0	0	0	0	0	0	0	٥
F. ( to un) (el')	-13.18574	-12.98113	-15,56407	-15,36407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15,35946	-15.35946
1; h, w) (cV)	-31,63533	-31,63544	-67,69451	-49.66493	-31,63533	-31.63537	-31,63537	-31.63535	-31.63537	-31,63535	-31.63535
E. (atom - atom, nixp', AO) (eV)	-1,44915	-1.65376	0		0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
E, (up) (cV)	-33.08452	-33.28912	-67.69450	-49.66493	-31.63537	-33.49573	-33.49375	-33.08452	-33.49373	-33.08452	-33.08452
w (10" rad/s)	12.0329	12.1583	14.9286	24.2751	24,1759	6,43699	66965.6	15.4846	9.43699	9.55643	9.55643
F. (aV)	7.92028	8.00277	16,40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
(ak)	-0.18420	-0.18631	-0,25552	-0.25017	-0.24966	-0.16515	\$1\$91.0-	-0.20896	-0.16515	-0.16416	-0.16416
Ē, (cV)	0.13663	0.16118	0,35532 (Eq. (13,458))	0,35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0,12312 [2]	0.17978	0.09944	0.12312 [2]	0.12312 [2]	0.12312 [2]
E. (e.V.)	-0.11589	-0.10572	-0,22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Fy (map) (61)	-33.20040	-33.39484	-67.92207	-49.80996	-31.70737	-33,59732	-35.49373	-33.24376	-33.59732	-33.18712	-33.18712
Emple, no no! (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
E (c. 10) (cV)	0	0	-13,59844	-13.59844	-13.59844	0	0	٥	0	0	0
Entires (cV)	3,95062	4,12506	12.49186	7.83016	3,32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

FOR U.S.	Value	30-3	20-0	7.7	77.2	A.J	10.00	170	13.0	1	1		-		
				É		=			(0)	(e)	<u>ت</u>	و د	Celculated	Experimental	Reinive
		665	days										Total Bond	Total Bond	Error
077	Pinnshul school			1									Energy (eV)	Energy (eV)	
200	Cume myr cuter	7	>	7	0	0	•	0	0	o	0	٥	32 R4496	11 907	P.100
O.H.O	Ethyl methyl other	-	_	F-3	-	•	_	0	0	c	-		46 10010		2000
Ç	Diethyl whee		•	r	•	•	•		•	,	•	,	200	20.00	3
2	Mark James Anders	• -	• •	•	•		7	>	>	0	•	0	57.54924	37.500	-0.000\$6
2017	ואכוואי לוסטלי מוום	-	-	2	7	c	~	0	٥	0	0	-	08751 65	237.62	00000
0 7	Saprapy methyl ether	-	-	•	•	_	-	•	•						
, E	Dinronal coloer		. •	. •				•	٠.	>	>	>	27.43369	57.499	0.00078
		> 1	•	•	•	5	₹	0	0	0	0	•	81.85464	\$1.817	-0.6005
2	Dissprapy and	o	,	4	•	<b>6</b> -1	0	⋖	0	-	-	~	67777	***	0.000
O'H'	t-Butyl ethyl ether	-	-	*	-	•				•	•	•	74000	090.75	2000
	One of the second second			, ,		>	_	•	-	0	0	•	82.10276	82.033	0000
	tenanta probudbàs crues	_	-	•	0	_	0	~1	_	c	c	•	26136	01770	
Q.	Dibutyl ether	c	۲.	·	<	•	4				•	•			
5	Diese hand other	, (				٠ د		>	>	5	0	•	106.18004	106.122	9000
2	היאנבי סחולו בחום	>	7	9	~	-1	~	4	0	0	0	0	106 38187	106 410	
Q	Di-t-buty ether	7	c	٠	-	<	<		•					2000	
C	Burn Sachund adam	٠.		٠,		٠.	>	>	•	3	>	•	106.65628	106.425	000
2011	Tarria Isponia Culti	_		•						•					

Table 13.68. The bond angle parameters of alkyl others and experimental values [1], in the calculation of heta, the parameters from the preceding angle were used. E, is  $E_r\{anon-anon, m, \mu^1, J(1)\}$ ,

	Τ.	8	B	7	T	1	Т	T	Τ		Ţ-	Τ-	<del></del>	7
Θ. Θ.	112 (dimethyl ether)	111.9 (ethyl methyl ether)	(chy) methy! chc?)	107 (breazinc)	112 (projume) 113.8 (bulano) 110.8	(butane) (butane) (11.4	(isobatane)			110.8 (Grobusne)		111.4 Geobatane)	111.4 Grahame)	
G. C	2	21.35	190 13	101.44	110.49	110.49	109.50	4.80	2.00	110.67	110.76	11.2	111.27	107.50
6,⊙									T				$\top$	T
e_ ©														
e, ©	<u> </u>		<u> </u>		18.31	15.09		70.56	70.56					72.50
E, (eV)	-1.R5R3K	-1.45836	1.65376	0			•			1,85836	•	•	-1,K\$B36	
٧,	0.78155	0,77649	0,x3473	1.15796			1.1573/6			0.81540	1,04897	1.04887	1,04887	
5	-	-	-	6.75			0.75			-	27.5	a.75	27.0	
ڻ	-	-	-	-			-			-	-	-	-	
ڻ	-	-	-	-			-			-	0.73	0.73	0.73	
ς. γ-12	0 72155	0,77699	0.83393 (Eq. (15.114))	-			-			0,81349	17716.0	17116.0	17716.0	
5° M	0.78155	4.77690	0.81549	0.R6339			0.KG359			0,81349	D.N.7495	0.87495	0.K7495	
Aton 2 Hydridizzion Dorignation (Toble 15.3.A)	Æ	¥	0	æ			=			n	-	-	-	
11. Aut. 2.	17,40369	-12,51099	-13 61806	τ			I			-16,68412	-14.82375	-1412373	-14.82575	
Atom 1 Hybridization Designation (Toble 15.3.A)	E.	Ŧ	25	7			-			ĸ	*0	~	۶	
Frankask Akm I	629025'41-	(4012.71.	-16.68413	.15.75473			-15.75403			-14,68412 C,	-15.55033	.15.55033	-13,53033 C,	
LC. Tembel Aven (a,)	4.4721	4.438.5	4.5607	3,433			3,4252			4.7958	4.1633	4,1633	4,795#	
(a, )	2,68862	2.67935	3,679.35	2.110%	,		2,00711			1,91547	2,11325	2.09711	2,90327	
# [ e	2.68862	241162	1,9(547	2,11106			11001		1	2,015.17	1,91547	2,91547	2.90327	
	α',οι', (ι', -ο (i))	A'' DC' $(C'_{\nu} - O'(0))$ $(C'_{\nu} - O'(0))$	((!) (\(\doldsymbol{\text{\tiny}\text{\tiny}\text{\tinit}\\ \text{\text{\text{\text{\text{\text{\text{\text{\teit}\tinitht{\text{\text{\text{\text{\text{\text{\text{\text{\texi}\text{\text{\text{\text{\text{\text{\text{\text{\text{\text{\tinit}\\\ \tinithting{\text{\text{\text{\text{\text{\text{\text{\tinit}}\\ \tittt{\text{\text{\text{\text{\text{\text{\text{\text{\text{\texi}\tilit{\text{\text{\text{\text{\text{\texi}\text{\tilit{\text{\texi}\text{\text{\texi}\text{\text{\text{\texi}\text{\texitt{\text{\texi}\text{\texitil\tii}\tittt{\tilit{\texitil\tii}\\\tii}\\tiint\text{\text{\texitilex{\tiint{\texitilex{\tiin}\	H, JHZ	'כנ"נ'נ'	H'S.JZ	H".H7	, , , , , , , , , , , , , , , , , , ,	H, 7, 12	#.C.C.	4C,C,H C,	H,7,7,7	ZC,C,C, un C,	7,1,1,7

PRIMARY AMINES 
$$(C_n H_{2n+2+m} N_m, n=1,2,3,4,5...\infty)$$

The primary amines,  $C_n H_{2n+2+m} N_m$ , comprise an  $NH_2$  functional group and a C-N functional group. The alkyl portion of the primary amine may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and 5 methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in primary amines are equivalent to those in branched-chain alkanes.

The primary amino  $(NH_2)$  functional group was solved using the procedure given in the Dihydrogen Nitride  $(NH_2)$  section. Using the results of Eqs. (13.245-13.368), the primary amino parameters in Eq. (15.52) are  $n_1 = 2$ ,  $C_1 = 0.75$ ,  $C_2 = 0.93613$  (Eqs. (13.248-13.249)), 15  $C_{1n} = 1.5$ , and  $c_1 = 0.75$ . In primary amines, the  $C2sp^3$  HO of the  $C - NH_2$ -bond MO has an energy of  $E(C,2sp^3) = -15.35946$  eV (Eq. (15.18) with s = 1 and Eqs. (15.19-15.20)) and the N AO has an energy of E(N) = -14.53414 eV. To meet the equipotential condition of the union of the N - H H<sub>2</sub>-type-ellipsoidal-MO with the  $C2sp^3$  HO, the hybridization factor  $c_2$  of Eq. (15.52) for the N - H-bond MO given by Eq. (15.68) is

$$c_2(H \text{ to } 1^\circ N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.35946 \text{ eV}} = 0.94627$$
 (15.115)

The C-N group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. In primary amines, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a 25 corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), and the N AO has an energy of  $E(N) = -14.53414 \, eV$ . To meet the equipotential condition of the union of the

C-N  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the C-N-bond MO given by Eqs. (15.68) and (15.70) is

$$c_2(C2sp^3HO\ to\ N) = \frac{E(N)}{E(C,2sp^3)}c_2(C2sp^3HO) = \frac{-14.53414\ eV}{-14.63489\ eV}(0.91771) = 0.91140 \quad (15.116)$$

 $E_T(atom-atom,msp^3.AO)$  of the C-N-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is  $-1.44915\,eV$ . It is based on the energy match between the N of the  $NH_2$  group and the  $C2sp^3$ . HO corresponding to the energy contributions to the single bond that are equivalent to those of methyl groups,  $-0.72457\,eV$  (Eq. (14.151)), where the N-H bonds are also energy matched to the C-N bond.

The symbols of the functional groups of branched-chain primary amines are given in Table 15.69. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of primary amines are given in Tables 15.70, 15.71, and 15.72, respectively. The total energy of each primary amine given in Table 15.73 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.72 corresponding to functional-group composition of the molecule. The bond angle parameters of primary amines determined using Eqs. (15.79-15.108) are given in Table 15.74.

Table 15.69. The symbols of functional groups of primary amines.

Functional Group	Group Symbol
NH <sub>2</sub> group	$NH_2$
C-N	C-N
CH₃ group	$C-H$ $(CH_3)$
CH₂ group	$C-H(CH_2)$
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Lable 13.70. The peointings bond parameters of primar											
Parameter	NH, Group	C-∧ Graup	C-H (CH <sub>3</sub> )	Growing Growing	C - H Group	Group	CC (b)	C~C (c) Group	C-C (d) Group	Group	C-C(f) Group
0 (0,)	1.28083	1.92682	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2,12499	2.10725	2.10725
$c'(a_a)$	0.95506	01886.1	1.04856	1.05553	1.05661	1.45744	1,45744	1,45164	1,45744	1.45164	1.45164
Bond Length 2c' (A)	1.0103	01697'1	1.10974	1.11713	1.11827	1.54280	1.54280	1,53635	1.54280	1.53635	1.53635
Exp. Bond Length (A)	1.010 (methylaminc)	1,473 (methylamine)	1,107 (C-H propane) (C 1,117 (C-H bulane) (C	1.107 (C-H propane) 1.117 (C-H butane)	1,122· (isobutane)	1.532 (propane) 1.531 (biltene)	1.532 (propane) 1.531	1.532 (propæne) 1.531	1.532 (propane) 1.531	1.532 (propano) 1.531	1.532 (propane) 1.531
h,c (a,)	0.85345	1.33634		1.29569	1.29924	1.54616	1.54616	1.52750	1.54616	1.52750	1.52750
b	0.74566	0.72041	0.63580	0.63159	0,63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

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Table 15.71. The M(	
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table 19.71. The INO to ITO microck Econemics bond parameters of printary and		יו המשוובונים ה		עייי א מוני	ics. A, h , A are a or dikyr groups, a, is a, quam - anom, my .AU).	. 6, 15 Er (010	יייי – מיניייי יייילט	.(2):								
Bond	Atom	127	£,	167	E <sub>T</sub>	Final Total	7	'hu	Ecreture	$E(C2sp^2)$	.8	6	9	ď,	d,	_
		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Cay Cay	(d.)	(°)	(eV) Final	(eV) Final	©	•	·©	(°)	(°)	
$H_iCN(H) - H$	Ν	-0.72457	0	0	0		0.93084	0.87495	-15,55033		118.00	62.00	87.59	0.54432	0.41075	т-
-H <sub>1</sub> C,N(H)-H	ν	-0,72457	0	0	0		0.93084	0.87495	.15,55033		118.00	62.00	28.20	0,54432	0.41073	τ-
H,C-NH,	U	-0.72457	0	0	0	-152.34026	0.91771	0 87495	-15.55003	-15,35946	85.28	94.72	40,73	1,46010	0.077200	_
H,C - NH,	2	-0.72457	0	0	0		0.93084	0.87495	-15.55033		85.28	94.72	40.73	1.46010	0,07200	_
-H,C, -NH,	ر.	-0.72457	-0.92918	0	0	153,26945	17716.0	0.82562	-16,47951	-16 28854	80.20	8.80	37.50	1,52858	0.14048	·
-H,C, -NH,	>	-0.72457	0	۰	0		0.93084	0.87495	-15.55033		85.28	94.72	40.73	1.46010	0.07700	58
(H (CH,)	Ü	-0.92918	0	0	0	-152.54487	0.91771	0.86359	-15.75493	-15.56407	47.49	102.51	41.48	123564	0.1870\$	, 
$(C-H(CH_{\xi}))$	C	-0.9291R	-0 92918	0	0	153,47406	17716.0	0.81549	-16.68412	-16.49325	08.47	11.53	35.84	135486	0.29933	
('-H (CH)	Ü	40.92918	-0.92918	-0.92918	0	-154,40324	0.91771	0.77247	-17,61330	-17,42244	61.10	118.90	11.37	1,42938	92675.0	_
$H_3C_sC_sH_4CH_1-$ ( $C=C_s(a)$ )	c,	-0.92918	0	0	۰	.132.54417	17716.0	0.86339	13.75493	-15.56407	63.82	116.18	30.08	97818.1	901850	
$H_jC_iC_kH_jCH_j-$ $\{C_i=C_iC_j\}$	ť.	81626'0-	11626.0-	0	0	-153,47406	0.91771	0.81349	-16.68412	-16.49325	36.41	65.031	26.06	1.90290	0.45117	,
$R = H_1C_1C_1(H_2C_2 - R^2)HCH_2 - (C - C_2(b))$	5	81626.0-	818Z6 O-	-0 92918	c	154 40324	177160	0.77247	-17.61330	-17.47244	48.30	131.70	21.90	191161	0.5138\$	<b></b>
$ (R - H_2C_4(R' - H_2C_2)C_4(R'' - H_2C_2)CH_3 - (C - C_2C_2) $	٠,٠	8 16220:0-	-0.72457	-0.72457	-0.72457	-154.71260	0.91771	0.73419	-17.92866	ett.:1-	48.21	67,181	21.74	1,95734	0.50570	···
$isoC_sC_s(H_sC_s - R^s)HCH_s - (C - C^s(d))$	ť	-0.92918	-0.92918	-0.92918	0	-154.40324	0.91771	0.77247	-17,61330	-17.42244	6.30	02.161	21,90	1,97162	0.51388	т
$ter(C_s(R-H_sC_s)C_s(R^n-H_sC_s)CH_s-(C-C(c))$	<b>'</b> '	-0.72457	-0,72457	0.72457	-0.72457	-154.51399	0,91771	0.76765	-17.92866	פתנת,רו.	50.04	129.96	977	1.94462	0.49291	,
$(e^{-C_{\alpha}}C_{\alpha}(H_{\alpha}C_{\alpha}-R)HCH_{\alpha}-C_{\alpha}(C))$	່ວ່	-0.72457	91626.0-	-0.92918	ó	.154.19863	1,7719	0.78155	-17.40869	.17,21783	52.78	27.72	20.02	1,92443	0.47279	~
$\lim_{t\to 0^+} (R - H_2^{C_s})C_s(R^n - H_2^{C_s})CH_2^{-n}$	ď	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	17716.0	0.76765	-17.97866	errer.r1-	X0.04	39.96	32.66	1,94462	0.49298	

Parameters NH <sub>1</sub> C-N ('H <sub>1</sub>	NH,	Group	(H.)	. H.	Group	C-C (a) Group	ربار (q) ونسله	(S) (S) (S) (S) (S)	Ganb Ganb	(e) day	Cardinal Cardinal
	Crodip		Cromp	Giona						-	-
n,	2	-	3	2	-	-	-	-	-	-	-
$u_{2}$	0	0	2	1	0	0	0	. с	0	0	0
11,	~	0	0	0	0	0	0	0	0	0	0
	0.75	0.5	6.75	0.75	0.75	5'0	5'0	5.0	\$"0	0.5	0.5
	0.93613	-	_	-		_	_	1	1	1	1
5	0.75	-	-	-	-	•	1	1	1	1	1
	0.94627	0.91140	0.91771	17716.0	0.91771	17716.0	17716.0	17216.0	17716.0	17716.0	17716.0
ť	0	0	c	-	-	0	0	0	-	-	0
6,	-	2	_	-	-	2	2	2	2	2	2
c,	2	0	3	2	-	0	0	0	0	0	0
-	1.5	0.5	0.75	0.75	0.75	0.5	0.5	5.0	5.0	5.0	0.5
	_	-	-	-	_	-	-	-		1	1
V, (eV)	-77.89897	-32.46339	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	21101.62-	-29.10112
V, (eV)	28.49101	9,80175	38.92728	25.78002	12.87680	9.33352	9.33352	9,37273	9.33352	9.37273	9.37273
r (eV)	30,40957	8.42409	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_ (aV)	-15.20478	-4.21204	-16,26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(x1 m) (aV)	-14.53414	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15,56407	-15,35946	-15.35946
Δίμισι ( v · m) (cV)	0	-1.44915	0	0	0	0	0	0	0	0	0
Ex (m m) (aV)	-14.53414	-13.18574	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15,35946	-15.35946
E(1, 10 10) (4V)	-14.53414	0	o	0	0	0	0	0	0	0	0
Er (11,200) (cV)	-48.73642	-31.63534	-67,69451	-49,66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_T \left( atom - atom, msp^3, AO \right) (eV)$	0	-1,44915	0	0	0	-1.85836	-1.85836	516441-	-1.85836	-1,44915	-1,44915
E, (w) (eV)	-48.73660	-33.08452	-67.69450	-49,66493	-31.63537	-33,49373	-33,49373	-33.08452	-33.49373	-33,08452	-33.08452
a (10" rad!s)	64.2189	18.9231	24.9286	1517.42	24.1759	9,43699	9.43699	15.4846	9.43699	9.55643	9.55643
Er. (eV)	42.27003	12.45552	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	651129	120679	6.29021
E. (cV)	-0.40690	-0.23100	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Ex. (aV)	0.40929	0.12944	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312	0.17978	0.09944 [5]	0.12312 [2]	0.12312 [2]	0.12312 [2]
E. (eV)	-0.20226	-0.16628	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Emy (cV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Erfeinmy) (cV)	-49.14112	-33,25079	-67.92107	96608'64-	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
E (4 11 10) (cV)	-14.53414	-14,63489	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489	14.63489	-14.63489	-14.63489	-14.63489
E (aV)	-13.59844	o	-13.59844	-13,59844	-13.59844	0	0	0	0	0	0
$E_{p}(tom_{p})$ (cV)	7.41010	3.98101	12.49186	7.83016	3.32601	4,32754	4.29921	3.97398	4.17951	3.62128	3,91734

Culculared Total Bond 23.8827 36.04067 48.19837 60.35607 60.45696 60.78863 60.78863 () 2-2 (e) 2-2 Table 15.73. The total bond energies of primary emines calculated using the functional group composition and the energies of Table 15.72 compared to the experimental values [3].

Founds

NH, C = N (H, CH, CH C = C (s) C = C (c) C = C (d) |   | Г                       |             |                  |                         |                           | ь                          | ٦         |   | -           |                   | Т           | _        |          |           |          | <b>—</b>          | -         |             | _        | _           |
|---|-------------------------|-------------|------------------|-------------------------|---------------------------|----------------------------|-----------|---|-------------|-------------------|-------------|----------|----------|-----------|----------|-------------------|-----------|-------------|----------|-------------|
|   | -                       | Œ           |                  | 107.1<br>(methylamine   | 110.3<br>(methylamine     | 101.0<br>(methylamine<br>) | (prepane) | (propere)<br>(13.8<br>(butane)<br>(10.8 | (isobutane) | (butane)<br>(11.4 | (isobutane) |          |          |           | 1.011    |                   |           | (isobutane) | 111.4    | (secondari) |
|   | Cal. 0                  | €           |                  | 108.40                  | 110.48                    | 108.44                     |           | 110.49                                  |             | 110.49            | 1           | 109,30   | 109.44   | 109.44    | 110.67   | 110.76            | T         | 77.111      | 111.27   |             |
|   | 9                       | · ©         |                  |                         | _                         |                            |           |   |             |                   |             |          |          |           |          |                   |           |             |          |             |
|   | 9                       | · ©         |                  |                         |                           |                            |           |   |             |                   |             |          |          |           |          |                   |           |             |          |             |
|   | 6                       | · ©         | 4                |                         |                           | <u> </u>                   |           | 89.51                                   |             | 16.91             |             |          | 70.56    | 70.56     |          |                   |           |             |          |             |
| ÷   | E,                      | (§)         |                  | •                       | 0                         | ٥                          |           |   |             |                   |             | ,        |          |           | -1.85836 | ٥                 |           | 0           | -1.85836 |             |
| atam, msp³.4C   | 25                      |             |                  | 1.05679                 | 0.97194                   | 1.15796                    |           |   |             |                   | 1.15796     |          |          |           | 0.81549  | 1.04887           |           | 1.0488)     | 1.04887  |             |
| Er (aram -  | ۍ<br>                   |             |                  | 6.73                    | 67.0                      | 0.75                       |           |   |             |                   | 0.75        |          |          |           | _        | 0.75              |           | 6.79        | 6.75     |             |
| used. E <sub>7</sub> is   | ڻ                       |             |                  | -                       | -                         |                            |           |   |             |                   | -           |          |          |           | _        | -                 | -         | -           | -        | 1           |
| angle were  | ט                       |             |                  | -                       | 87.0                      | -                          |           |   |             |                   | -           |          |          |           | -        | 6.73              | Ę         | 2.5         | 27.0     |             |
| he preceding  | Մ                       | Atom 1      |                  | -                       | 0.88583                   | _                          |           |   |             |                   | _           |          |          |           | 0,81549  | 17716.0           | 122700    |             | 0.91771  |             |
| rameters from   | ·5                      | Vietn I     |                  | 0.94627<br>Eq (15.115)) | 0.91140<br>(Eq. (15.116)) | 0.86359                    |           | -                                       |             |                   | 0.86359     |          |          |           | 0.81349  | 0,87495           | 0.17495   |             | 0.17495  | 1           |
| tallon of e, the p  | Atom 2<br>Hybridization | Designation | (1) able 13.3.A) | ×                       | z                         | <b>=</b>                   |           |   |             |                   | H           |          |          |           | 25       | -                 | _         |             | -        |             |
| 11 III C.   | E.                      |             |                  | Ξ.                      | -15.35946                 | ,я                         |           |   |             |                   | æ           |          | 1        | -16 68413 | ن        | -14.82575         | -14,82575 | -           | -14.1355 |             |
| The parameters from the preceding angle were used. $E_{\rm p}$ is $E_{\rm p}$ (aron – aron, map $^2$ AO | I fybridization         | Designation | 0.00             | 2                       | 5                         |                            |           |   |             |                   |             |          |          |           | R        | ~                 | ~         |             | 'n       |             |
|   |                         | \$ 12 E     |                  | -14.53414               | -14.53414                 | -13.75493                  |           |   |             |                   | -15.75493   |          |          | -16.68412 | ن .      | -15.55033<br>C.   | -15.55033 |             |          |             |
|   | Jenius L                | Nems ( a, ) |                  | 3.0924                  | 3.8816                    | 3,4252                     |           |   |             |                   | 3,4252      |          |          |           | 4.7958   | 4.1633            | 4,1633    |             | 4.7058   |             |
|   | 3 7                     | (a)         |                  | 1.91013                 | 1,77620                   | 2,11106                    |           |   |             |                   | 2,09711     |          |          |           | 2.91547  | 211323            | 11700.2   |             | 2.90327  |             |
|   | Il Marie C              | (°)         |                  | 1.91013                 | 1,91013                   | 2.11106                    |           |   |             |                   | 2.09711     |          |          |           | 291547   | 2.91547           | 2.91547   |             | 1.90327  |             |
| Alosu of Argle  | ,                       |             | , mm,            | ביווים                  | ZHW."                     | Moth has<br>ZHC, H         |           |   |             | H':5'.77          | Н."Н        | 7,7,7,77 | H'.5'.37 | 75.5.75   | ů<br>E   | ZC, Z, H<br>(', H | H':5'.37  | 7:1:0       | , '' E   | 7.5.7.7     |

Table 13.74. The bond angle parameters of primary amines and experimental values [1]. In the calculation of 0,, the parameters from the precedi

## SECONDARY AMINES $(C_n H_{2n+2+m} N_n, n=2,3,4,5...\infty)$

The secondary amines,  $C_n H_{2n+2+m} N_m$ , comprise an NH functional group and two types of C-N functional groups, one for the methyl group corresponding to the C of C-N and the other for general alkyl secondary amines. The alkyl portion of the secondary amine may 5 comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in secondary amines are equivalent to those in branched-chain alkanes.

The secondary amino (NH) functional group was solved using the procedure given in the Hydrogen Nitride (NH) section. Using the results of Eqs. (13.245-13.316), the secondary 15 amino parameters in Eq. (15.52) are  $n_1 = 1$ ,  $C_1 = 0.75$ ,  $C_2 = 0.93613$  (Eqs. (13.248-13.249)),  $C_{1o} = 0.75$ , and  $c_1 = 0.75$ . In secondary amines, the  $C2sp^3$  HO of the C-NH-bond MO has an energy of  $E(C,2sp^3) = -15.56407 \, eV$  (Eqs. (14.514-14.516)); Eq. (15.29) with s=1 and s=2, Eq. (15.31), and Eqs. (15.19-15.20)) and the N AO has an energy of  $E(N) = -14.53414 \, eV$ . To meet the equipotential condition of the union of the N-H  $H_2$ -20 type-ellipsoidal-MO with the  $C2sp^3$  HO, the hybridization factor  $c_2$  of Eq. (15.52) for the N-H-bond MO given by Eq. (15.68) is

$$c_2(H \text{ to } 2^{\circ}N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.56407 \text{ eV}} = 0.93383$$
 (15.117)

The C-N group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. In secondary amines, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), and the N AO has an energy of  $E(N) = -14.53414 \, eV$ . To meet the equipotential condition of the union of the

C-N  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the C-N-bond MO given by Eq. (15.116) is  $c_2(C2sp^3HO to N) = 0.91140$ .

As given in the Continuous-Chain Alkanes  $(C_n H_{2n+2}, n=3,4,5...\infty)$  section, each methylene group forms two single bonds, and the energy of each  $C2sp^3$  HO of each  $CH_2$  group 5 alone is given by that in ethylene,  $-1.13379 \, eV$  (Eq. (14.511)). In secondary amines, the N of the NH group also binds to two  $C2sp^3$  HOs and the corresponding  $E_T(atom-atom, msp^3.AO)$  of each C-N-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is  $-1.13379 \, eV$ . It is based on the energy match between the N of the NH group to the two  $C2sp^3$  HOs corresponding to the energy contributions to each of the two single bonds 10 that are equivalent to those of independent methylene groups,  $-1.13379 \, eV$  (Eq. (14.511)), where the N-H bond is also energy matched to the C-N bonds.  $E_T(atom-atom, msp^3.AO)$  of the C-N-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is  $-1.13379 \, eV$ . It is based on the energy match between the N of the NH group to two  $C2sp^3$  HOs corresponding to the energy contributions to the single bond that are equivalent to those of methyl groups,  $-0.72457 \, eV$  (Eq. (14.151)), where the N-H bonds are also energy matched to the C-N bond.

The symbols of the functional groups of branched-chain secondary amines are given in Table 15.75. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of secondary amines are given in 20 Tables 15.76, 15.77, and 15.78, respectively. As in the case of  $NH_2$  (Eq. (13.339)),  $C_{1o} = 2C_1$  rather than  $C_{1o} = C_1$  in Eq. (15.52) for the C - N bond. The total energy of each secondary amine given in Table 15.79 was calculated as the sum over the integer multiple of each  $E_D$  (Group) of Table 15.78 corresponding to functional-group composition of the molecule. The bond angle parameters of secondary amines determined using Eqs. (15.79-15.108) are given in Table 15.80.

Table 15.75. The symbols of functional groups of secondary amines.

Functional Group	Group Symbol
NH group	NH
C-N (methyl)	C-N (i)
C-N (alkyl)	C-N (ii)
CH₃ group	$C-H\left(CH_{3}\right)$
CH₂ group	$C-H(CH_2)$
CH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Table 15.76.	The geometrical bo.	Table 15.76. The geometrical bond parameters of secondary amines an	undary amines and e	id experimental values [1	<u>:</u>							
Parameter	Group	Group	C-N (ii) Group	$C-H(CH_3)$ Group	C-H(CH <sub>3</sub> )	Group	C = C (a) Group	C-C(b) Group	C-C (e) Group	C-C (d) Group	C-C (e)	C-C()
g (a)	1,26224	1.94862	1.94862	1.64920	1.67122	1.67465	2.12499	2,12499	2.10725	2 12499	2 10724	20701.0
c. (a)	0.94811	1,39593	1,39593	1.04856	1.05553	1.05661	1.45744	1,45744	145164	1 45744	1 18164	. 46161
Bond Length 2c' (A)	1.00343	1.47739	1.47739	1.10974	1,11713	1.11827	1,54280	1.54280	1.53635	1.54280	1.53635	1.53635
Evn Bond				-								
Length Ength	1.00 (dimethylamine)	1,455 (dimethylamine)		(C-H propane)	ne) (C ~ H propane)	1.122 (isobutane)	1,532 (propane) 1,531	1.532 (propæne) 1.531	1.532 (propane)	1,532 (propane)	1.532 (propane)	1.532 (propane)
				(C-H butane)	(C-H butane)		(butane)	(butane)	(hutane)	1cc.1	1531	1.531
n.c. (a,)	0.83327	1.35960	1.35960	1.27295	1.29569	1.29924	1.54616	1,54616	1.52750	1 \$4616	1 C7750	(burane)
5	0,75113	0.71637	0.71637	0.63580	0.63159	>00590	O ARKAA	007670	000000		00000	00/201
						0,000,0	O'DOO'O	0.08000	0.68888	0 68600	000070	000070

Bond	Ающ	1,1	E,	$R_T$	f. <sub>T</sub>	Final Total	7.6	1	Eratum	16(0)20	.0	9	a	,	,
		Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	C.2-m	(%)	(%)	(cV) Final	(eV)	ε		E	, (°)	, (°)
H,C,N(C,H,)-H	2	-0.56690	-0.56690		•	Ş	100								
-H.C.N(R, N-H	>	0.66600	0 44450				033084	0.83232	-15.95954		118,18	61.82	64.60	0.54546	0.40264
HC -NH-CH	: :	CONCE	-0.30030	,	8		0,93084	0.85252	-15,95954.		118.18	61.82	\$	0.54546	0.40264
1.30° 1111 - C.113	-	-0.56690	٥	0	0	-152.18259	111160	0.81392	-15.39265	-15.20178	84.14	95.86	02.07	14808	CENTOO
n,cwn -c.n,	>	-0.36690	-0.56690	0	0		0.93084	0.65252	-15.95954		1095	90 00			Zenen'n
-n,c,-NH -C,R	ن	-0.56690	-0.92918	0	0	-453,11177	17716.0	0,83360	-16,32183	-16 13097	78.89	12.00	2 8	90000	015415
-4,C,-NH-C,H,-	2	-0.56690	-0.56690	٥	0		0.93084	0.85252	-15,95954		\$0.05	\$6.00	30.35	Ocace.	0.19037
C - H (CH <sub>3</sub> )	ن	-0.92918	0	۰	0	-152.54487	17710.0	0,86359	-15.75493	-15.56407	7.48	19 201	8 18	900CC	or 13415
C-H (CH,)	٠	-0.92918	-0.92918	٥		-153.47406	17710	0.81549	-16.68412	-16 49725	619	5		50	0.10
C - H (CH)	ن	-0.93918	-0,92918	-0.92918	•	-154,40324	12.60	0.777.0	011171	1			19.50	1.33486	0.29933
H,C,C,H,CH,-	ن	-0.92911	۰			10000			200		al. Id	114.90	TE IE	1,42988	0.37326
H.C.H.CH. ~	·				,		111111111111111111111111111111111111111	0.46339	-13,73493	-15.56407	63.82	16.18	30,01	1.83879	0.38106
('-('(a))	C,	-0.92918	-0.92918	0	0	-153,47406	0.91771	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90890	0.45117
$R-H_3C_3C_3(H_3C_3-R^2)HCH_3 (C-C_3(b))$	ť	-0.92918	11626'0-	-0.92918	o	-154,40324	0.91771	0.777.47	-17.61330	-17.42244	41.30	131,70	21 90	1 07163	0 61389
$R - H_3C_s(R' - H_2C_s)C_s(R' - H_2C_s)CH_1 -$	ئن	-0.92918	-0.72457	-0.72457	-0.72457	0912 451.	124.100	00000	27000	1					2000
100 (H C = n) HCH =									00076')	-17.13719	48.21	e. E:	21.74	1.95704	0.50570
(C-C(d)	*ن	-0.92918	-0.92918	816Z6.D-	•	-154,40324	17716.0	0.77247	-17.61330	-17,42244	48.30	57.151	21.90	1,97162	0.51388
$ienC_s(R'-H_2C_s)C_s(R''-H_2C_s)CH_2 - (C-C'(e))$	ť	-0.72457	-0.72457	-0.72457	-0.72457	-154 51399	17116.0	0.76765	-17.92866	er. t. r. s. r. s	50.08	129.96	22.66	1.94462	0.49298
$leriC_sC_s(H_sC_s - R^s)HCH_s - (C_s - C_s(f))$	ť	-0.72457	-0.92918	-0.92918	٥	-154,19863	17716.0	0.78155	-17.40869	-17,21783	52.78	17.11	2 2	1,9240	0.47279
$isoC_{*}(R-H_{!}C_{*})C_{*}(R^{*-}H_{!}C_{*})CH_{3}-(C_{!}-C_{!}(0))$	ڻ	-0.72457	-0.72457	-0.72457	-0.72457	-154,51399	(7716.0	0.76763	-17.92866	47.73.TP	50.04	129.96	22.68	29776	0.49308

, atameters	Group	C~N (i) Granp	C - N (ii) Group	₹,	₹ 8	C-H Crown	C-C(a) Group	(e) U-U	Green Green	Guin	(e) (c) (c) (c)	(E) (E)
				Cronip	Group							
u'	-	-	_	_	7	-	-		-	-	-	-
n,	0	0	0	2	1	0	0	0	0	0	0	0
π,	0	0	0	0	0	0	0	0	0	0	0	0
	0.75	0.5	5.0	52.0	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C <sub>2</sub>	6.93613	1	1	1	-	_	_	-	-	-	-	-
6,	0.75	-	-	-	-	-	_	_	-	-	1	-
5	0.93383	0.91140	0,91140	0.91771	0.91771	0.91771	17716.0	177160	0.91771	17710	17719.0	17716.0
6,	-	0	. 0	0	1	1	0	0	o	-	-	0
r.		2	2	1	1	-	. 2	2	2	2	2	2
C <sub>5</sub>	-	0	0	3	2	ı	0	0	0	0	0	0
(,	0.75	_	_	22.0	0.75	0.75	0.5	5.0	0.5	0.5	0.5	2.0
C3.	-	-	-	-	1	-	-	_	-	-	-	-
V, (aV)	-39.21967	-31.98456	-31.98456	-107,32728	-70,41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (aV)	14,35050	9.74677	9.74677	38.92728	25.78002	12.87680	9,33352	9.33352	9,37273	9.33352	9.37273	9.37273
7' (eV)	15.53581	8.20698	8.20698	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V. (oV)	-7.76790	4.10349	4.10349	-16.26957	-10.53337	16242.8-	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(.m m) (aV)	-14.53414	-14.63489	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15,35946
$\Delta E_{H_2,m}(\omega,m)$ (oV)	0	-1.13379	-1.13379	0	0	0	0	0	0	0	0	0
Er (.w) 110) (eV)	-14,53414	-13.50110	-13.50110	-15.56407	-15,56407	-14.63489	-15.56407	-15.56407	15.35946	-15.56407	-15,35946	-15.35946
E. (4,300) (4V)	-31,63541	-31.63540	-31.63540	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31,63535	-31.63537	-31,63535	-31,63535
$E_r(ann-ann, asp^3, AO)$ (eV)	0	-1.13379	-1.13379	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
Er (sm) (eV)	-31.63537	-32,76916	-32,76916	-67,69450	-49.66493	-31,63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω (10" rad /.s)	47.06%	15.1983	26.0778	24.9286	24.2751	24.1759	9,43699	9,43699	15.4846	9.43699	9.55643	9.55643
Fr (aV)	30.98202	10.00377	17.16484	16,40846	15.97831	15.91299	6.21159	6,21159	10,19220	6.21159	6.29021	6.29021
E, (uV)	-0.34836	-0.20505	-0.26859	-0.25352	-0.25017	-0.24966	-0.16815	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Erm (aV)	0.40696	0.12944	0.11159	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13,458))	0.12312 [2]	0.17978	0.09944 [S]	0.12312 123	0.12312	0.12312
E (cV)	-0.14488	-0.14033	-0.21280	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Eng (cV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E, (ina) (c/)	-31.78025	-32.90949	-32,98196	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
Emma (r v. m) (cV)	-14.53414	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489
5 (n. 12) (a.V.)	-13.59844	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
E., (Gruss) (CV)	3.50582	3.63971	3.71218	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

C-C(A) Table 15.79. The total band energies of secondary annines colculated using the functional group composition and the energies of Table 15.78 compared to the experimental values (3).

Fromula Name HH C - N (i) C - N (ii) CH, CH, CH, CH, CH, CH (a) C - C (b) C - C (c) C - C (c) C - C (c) C - C (c)

					· · · · · · · · · · · · · · · · · · ·	HIC CONTRIBUTE	. The parameters from the preceding angle were used. E. is E. Glom and AO.	יחפוכיז ניסוח זו	he proceding a	angle were u	sed, E. is	E alom-	atom men A	<u> </u>					
	2c' Umd I (a <sub>b</sub> )	2c' Dend 1 ( a, )	2c' Tomains Aireas ( a, )	Frinkenske Or E Adem I	Atom I Hybridzation Designation	Erman Aions 2	Atom 2 Hybridization Designation	C <sub>1</sub>	C3 Abm2	Ů.	5	· c	35	$\frac{E_r}{(eV)}$	ø, ©	0-0	9 (0)	Cal. $\theta$ Exp. $\theta$ (°)	0 _
$\begin{array}{c} ZHCN\\ (C-N\ (i)\ \&\ (ii)) \end{array}$	1,09711	2 79186	4,0661	-14.82575	z	-14.53414	(ALCO PIGE)	0.91771	0.93383	0.75		1.0	732.10	,		$\dagger$	+	_	
ZHINC.	1.89621	2.701gK	18131	73.07	,	-15.36407		0,91140	Eq. (15.117))	$\perp$	$\cdot \mathbb{I}$		1,01,08	0		1	-	111.76 (dimethylamine)	amine)
(C-N (i) & (ii)			718.5	-16.33414	,	(15.117))	z	(15.116))	0.87418	۶.2 د	_	0.75	0.95917	0				107.27 Cdimethyloniae	,
(C-N (i) & (ii)	2,79186	2.79186	4.6260	-17.04640	62	-17,04640	29	0.79816	0.79816	-	-	-	0.79816	A1828 L-		$\dagger$	+	_	
McOn lens	2.11106	2.11106	3,4252	-15,73493	, ,	H	ж	0.86339	-	-	:	0.75	1.15796	0		+	= =	(dimethylamine) 107 108,44 (dimethylamine)	smine)
															1		_		ê
<i>בכ"כ"כ</i> "							,						·		69.31		=	112 (propane) 110.49 (butane)	_ E = E -
;																-	-	(isobuta	. e
May!															15.69	-	=	111,0 (bulana 111,4	o 🗈 -
H, JHZ	2.09711	2.09711	3.4252	-15.75493		æ	×	0.86359	-	1	-	27.0	14794			+	+	_	
'.)'.)'.'77													21011	,			2	109.30	
ZC,C,H										1	1				70.56		10	109,44	
אניניני. אניניניני	2.91547	2,91547	4.7958	-16.68412	25	-16.68412	ន	97.50	3	-	1.				70.56	+	2	109.44	
H'.J'.)7				-15.55033		7, 14						-	0.81349	-1,85836			=	110.67 (sobutane)	<u> </u>
	2.91547	2.11323	4.1633	u'		<u>ن</u>	_	0.87495	0.91771	0.75	_	6.75	1.04887	0		_	=	7201	
∠C,C,H ™ C,	2.91547	2.09711	4,1633	.(5.5503) .7.	-	-14,82575 C.	-	0.87495	0.91771	57.0	-	2,0	1.04887			+			
ZC,C,C,	721067	2,90327	4.7958	-15.53033	~	-14.82575	-	0.87495	12/16/20	- 5	-	, a				+			ē
ZC.C.C.				+		,						}	1000	-1.83836			111.27	27 (isobutane)	9

## TERTIARY AMINES $(C_n H_{2n+3} N, n = 3,4,5...\infty)$

The tertiary amines,  $C_nH_{2n+3}N$ , have three C-N bonds to methyl or alkyl groups wherein C-N comprises a functional group. The alkyl portion of the tertiary amine may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise 5 methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2CH)$  and t-butyl  $((CH_3)_3C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in tertiary amines are equivalent to those in branched-chain alkanes.

The C-N group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy.

15 In tertiary amines, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), and the N AO has an energy of  $E(N) = -14.53414 \, eV$ . To meet the equipotential condition of the union of the C-N  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the C-N-bond MO given by Eq. (15.116) is  $c_2(C2sp^3HO to N) = 0.91140$ .

As given in the Continuous-Chain Alkanes  $(C_n H_{2n+2}, n=3,4,5...\infty)$  section, the energy of each  $C2sp^3$  HO must be a linear combination of that of the  $CH_3$  and  $CH_2$  groups that serve as basis elements. Each  $CH_3$  forms one C-C bond, and each  $CH_2$  group forms two. Thus, the energy of each  $C2sp^3$  HO of each  $CH_3$  and  $CH_2$  group alone is given by that in ethane,  $-0.72457 \ eV$  (Eq. (14.151)), and ethylene,  $-1.13379 \ eV$  (Eq. (14.511)), respectively. In order to match the energy of the component HOs and MOs for the entire molecule, the energy  $E_{T_{oldow}}\left(C-C,2sp^3\right)$  given as a linear combination of these basis elements is  $-0.92918 \ eV$  (Eq. (14.513)). In tertiary amines, the N binds to three  $C2sp^3$  HOs and the corresponding  $E_T\left(atom-atom, msp^3.AO\right)$  of each C-N-bond MO in Eq. (15.52) due to the charge donation

from the C and N atoms to the MO is  $-0.92918 \, eV$ . It comprises a linear combination of the energy for a primary amine,  $-0.72457 \, eV$  and a secondary amine,  $-1.13379 \, eV$ .

The symbols of the functional groups of branched-chain tertiary amines are given in Table 15.81. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and 5 energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of tertiary amines are given in Tables 15.82, 15.83, and 15.84, respectively. The total energy of each tertiary amine given in Table 15.85 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.84 corresponding to functional-group composition of the molecule. The bond angle parameters of tertiary amines determined using Eqs. (15.79-15.108) are given in Table 15.86.

1. . . . .

(a) (c) (c) (d)
-----------------

	0-2	Group		2.10725		1.45164	319131		1.532	(propane)	1551	Contalle	1.52750	
	(e) C-C	Group		2,10725		1.45164	1,53635		1.532	(propane)	(butune)		1.52750	
	(p)	Group		2.12499		1.45744	1.54280		1.532	(propane)	(butane)		1.54616	
	(9),2-0	diero	-	2.10725	176161	1.43104	1,53635		1.532	1.531	(butme)	02463	06176.1	00007 V
	((b)	dipolip	יייייייי	4.124.99	1 45744		1.54280		1.532	1.531	(butane)	1 54616	ייייייי	O KRKOO
	(: - (: (a)		2 17490		1.45744		1.54280		(propane)	1.531	(Dufane)	1.54616	2000	0.08000
	Group		1.67465		1.05661		1,11827		1.132	(isobutane)		1.29924	D Ganne	0.000.0
7	(-H (CH <sub>2</sub> )	Oron	1.67122		1.0555.1		61711.1	1 107	(C-1		2000	1.69309	0.63159	
1 (21)	Group	1000	0.04720	10000	Drato.		1.10974	1.107	(C-H propane)	(C-/f butane)	1 27306		0.63580	
٥-١٧	Group	1 04313	CI CO.	1 40117			1.48188		1.458 (trimethylamina)	,	1,37505		0.71372	
Parameter		0 (0)		c. (a)		Rond	2c. (4)	Exp. Bond	Cengifi	(2)	h.c (a,)		y	

Bond	Atom	,		ii Einel Total		Einel Total									
		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy C2.p <sup>2</sup>	) <u>e</u>	(a)	Final Co	E(C22p²)	. C	e, ©	e. ©	(a <sub>0</sub> )	(°)
N-(C,H,),	Ü	-0.46459		.   0	°	(eV)	1221	18088	15 2000	1,11,000		1			
N-(C,H3),	, 5	-0.46459	-0.46459	-0,46459	·		0.93084	0.81815	ייסוניאו	04660.51	/F70	70.03	40.00	1.50312	0.10271
N-(C,H,-),	ن	-0.46459	11626'0-	٥	٥	-153,00946	177190	0.83885	13016 31-	2) K m 8(4	20.00	90100	20.00	COC.	0.17413
N-(C,H,-),	>	-0.46459	-0.46459	-0,46459	٥		0.93084	0.83885	-16.21953		70 %	25 101	30.04	2000	0.17413
С-н (сн,)	C	-0.92918	0	۰	٥	-152.54487	0.91771	0.86359	-15.75493	-15.56407	77.49	102.51	41.48	123564	0.18708
$C-H(CH_2)$	C	-0.92918	\$1626.0-	٥	۰	-153.47406	17716.0	0.B1549	-16.68412	-16.49325	68.47	111.53	35.84	1,35426	0.29933
C-H (CH)	į	-0.92918	.0.92918	1626.0-	۰	-154.40324	17716.0	0.77247	-17,61330	-17,42244	61.10	118.90	11.17	1 47988	2000
$H_1C_1C_1H_2CH_2 - (C_1-C_1)$	ີ	-0.92918	۰	0	٥	-152,54487	17716.0	0.86359	-15.75493	-15,56407	63.82	116.18	30.08	1.83879	0.38106
$H_i^{C,C,H_i}(H_i - (C - C (a)))$	5	-0.92918	-0.92918	0	o	-153,47406	17712.0	0.81549	-16.68412	-16.49325	56.41	123.59	26.06	1.90820	0.45117
$R = H_2 C_a (H_2 C_c - R^a) H C H_2 - (C - C^a)$	ť	-0.92918	\$1626.0-	-0.92918	۰	-154.40324	17116.0	0.77347	-17,61330	-17,42244	48.30	131.70	21.90	1.97162	0.51388
$R - H_2 \mathcal{L}_s(R^* - H_2 \mathcal{L}_s) C_s(R^* - H_2 \mathcal{L}_s) C_H_2 - (C - C \cdot C)$	ಚ	81626.0-	-0 72457	-0.72457	-0,72457	.154.71860	17716.0	0.75889	-17.92866	9.77.71-	48.21	131.79	21.74	N5734	0.50570
$lsmC_sC_s(H_3C_s-R)HCH_2 (C-C^*(d))$	ť	0.92918	81626.0-	11626'0-	۰	-154,40324	17718.0 .	0.772A7	-17.61330	-17,42244	48.30	131.70	21.90	1.97162	0.51388
$ler(C_s(R^n - H_sC_s)C_s(R^n - H_sC_s)CH_s - (C_s - C_s))$	ť.	-0,72457	-0.72457	-0.72457	-0.72457	-154,51399	17716.0	0.76765	-17.93866	-17.73779	\$0.04	129.96	22.68	1.94462	0.49293
$ler(C,C,\{H,C,-R'\}HCH_2-\{C,-C',\{I\}\}\})$	٠;	-0.72457	81626'0-	81626:0-	۵	154.19863	17716.0	0.78155	-17.40169	.17.2.1713	52.78	17.72	24.04	1.92443	0.47279
$i\kappa C_s(R'-H_2C_s)C_s(R''-H_3C_s)CH_2-$ $(C-C_s(0))$	ť	-0.72457	-0,72457	-0.72457	-0.72457	-154.51399	17716.0	0.75765	-17.92866	ert.cr.r1-	59,08	122.96	22.66	1.94462	0 49298

. .

Parameters	N-0	C-N CH CH	H.S	#-5	(1)	(J-C)	(a) (j - j)	(P) (J-)	(a) 0-0	Q-0
	Group	Group	Group	Group	Group	Group	Growp	Group	Group	Group
n <sub>1</sub>	-	3	. 2	1	-	-	_	-	-	-
n,	0	2	}	0	0	0	c	0	0	٥
n,	0	0	0	0.	0	0	0	0	0	0
C,	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
C,	-	-	-	1		1	-	1	-	-
6,		-	1	-	-	-	-	1	-	-
۶,	0.91140	0.91771	17710	17716.0	17716.0	0.91771	0.91771	0.91771	0.91771	17716.0
ç	0	0	1	1	0	0	0	r	-	٥
د.	2	1	1	1	2	7	2	2	2	7
<i>c</i> ,	0	3	2	1	0	0	0	0	0	٥
C,	0.5	0.75	0.75	0.75	0.5	5'0	5.0	0.5	5.0	0.5
. ,	-	1	1	1	1	-	1	ı	-	-
V, (cV)	-31.67393	-107.32728	-70,41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	9.71067	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (aV)	8.06719	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V. (cV)	-4.03359	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3,45250
E(.n no) (cV)	-14.63489	-15.56407	-15.56407	-14,63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15.35946
$\Delta \mathcal{E}_{\mu_3,\Omega}(m,m)$ (eV)	-0.92918	0	0	0	0	0	0	0	0	0
E, (10 m) (eV)	-13.70571	-15.56407	-15,56407	-14,63489	-15.56407	-15.56407	-15,35946	-15,56407	-15.35946	-15,35946
$E_r(n,\omega)$ (cV)	-31.63537	-67.69451	49.66493	-31,63533	-31.63537	-31.63537	-31,63535	-31.63537	-31.63535	-31.63535
$E_r(a_{lin} - a_{lin}, m_p^3, AO) (eV)$	-0.92918	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1,44915
$\mathcal{L}_{T}(s, r_{0}  (eV)$	-32,56455	-67.69450	-49,66493	-31.63537	-33.49373	-33,49373	-33,08452	-33.49373	-33.08452	-33.08452
w (10" rod/s)	18.1298	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9,55643
$\mathcal{E}_{K}\left( uV ight)$	11.93333	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
Eo (cV)	-0.22255	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	968020-	-0.16515	-0.16416	-0.16416
Frm (cV)	0,12944	0.35537 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978	0.09944	0.12312	0.12312	0.12312
E. (eV)	-0.15783	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E (aV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803
Er (time) (teV)	-32.72238	-67.92207	-49.80996	-31.70737	-33.59732	-33,49373	-33.24376	-33.59732	-33.18712	-33,18712
Emma (c. 17 117) (aV)	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
E (c. 17 1.7) (cV)	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
Entirmy (cV)	3.45260	12,49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734
								1		

Table 15.85. The total band energies of tertiary antires calculated using the functional group composition and the energies of Table 15.84 compared to the experimental values [3].

Formula Name C-N CH, CH, CH, CH, CH C-C (a) C-C (b) C-C (c) C-C (d) C-C (e) C-C (f) C-C (f) 000

2c' 2c' C'	Turning Ages France Hybridge Control of	Firebook Hybridenics Presented	Atom i Remodellion	In the second		Alom 2	iers from the	preceding ang	le were used	Er is Er	atom – at	$E_r$ is $E_r(alan - alam, msp', AO)$ $C_r$ $c_r$ $c_r$ $c_r$					L	
Somul ( C <sub>0</sub> ) Som	Uomili ( a, )		Aless f	Designation (Table 15.3.A)	Allem 2	Nyordization Designation (Table 15.3.A)	- N	Aen 2	Γ	5	٠.		(e v 7	. O	• ©	 		a.c.
2.80224	2 80224	4,6043	-17.14871	-	-17,14871	9	0.79340	0,79140	-	_	-	0.79340	-1.83836		-	=	110.48 (nimed	110.9
	2.11106	3.4252	-15.73493	۲	x	=	0.86359	_	-	-	0.75	1.15796	°			=	108.44 (dimed	107 hylamine) 107
														69.51	<b> </b>	<u> </u>	(p) (b) (10.49	(propare) 112 (propare) 113.8 (buzne) 110.8
														69.51			(150) (10,49 (150)	hutane) 11.0 11.4 utane)
$\neg$	7.0971	3.4252	-15.75493	7	×	×	0.86139	-	-	-	0.75	1.15796	o		-	<u>≅</u>	109.50	
_														70.56		109	109.44	
i –			-1668412		.16 60417									70.56		109,44	3	
	2.91547	4,7958	, t	ล	ئن ئا	· 83	0.81549	0.81549	-	-	-	0.81549	-1,85836			110,67	<u> </u>	110.8
	211323	4.1633	-15.55033 C.	•	-14.82575 C,	-	0.87495	17716.0	0.73	-	0.75	1.04887	0		+-	110.76		unanci
	2.09711	4.1633	-15.55033 C.	\$	-14.82575 C,	-	0.17495	17716.0	0.75	-	0.75	1.04887	0		$\dagger$	111.27	-	111.4
	2.90327	4.7958	-15.55033 C <sub>4</sub>	8	-14.82575 C,	-	0.17495	0.91771	0.75	-	0.75	1.04887	-1.85836		+	11137	+-	111.4
																-	4	ague)

Table 15.86. The bond angle parameters of tertiary

ALDEHYDES  $(C_n H_{2n} O, n = 1, 2, 3, 4, 5...\infty)$ 

The alkyl aldehydes,  $C_n H_{2n}O$ , each have a HC = O moiety that comprises a C = O functional group and a CH functional group. The single bond of carbon to the carbonyl carbon atom, C - C(O)H, is a functional group. In addition to the C = O functional group, formaldehyde comprises a  $CH_2$  functional group. The alkyl portion of the alkyl aldehyde may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C - C bonds can be identified. The n-alkane C - C bond is the same as that of straight-chain alkanes. In addition, the C - C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C - C bonds comprise functional groups. The branched-chain-alkane groups in aldehydes are equivalent to those in branched-chain alkanes.

The CH functional group was solved in the Hydrogen Carbide (CH) section except that  $E_{mag}$  is not subtracted since unpaired electrons are not created with fragmentation of the CH functional group of aldehydes. The  $CH_2$  functional group of formaldehyde is solved in the Dihydrogen Carbide  $(CH_2)$  section except that the energy of each C-H MO is matched to the initial energy of the  $C2sp^3$  HO (Eq. (15.25)). The C=O and C-C(O)H groups are solved by hybridizing the 2s and 2p AOs of each C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the O AO or between two  $C2sp^3$  HOs, respectively, to form a MO permits each participating orbital to decrease in radius and energy. In alkyl aldehydes, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)) and the O AO has an energy of  $E(O) = -13.61806 \, eV$ . To meet the equipotential condition of the union of the C=O H<sub>2</sub>-type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the C=O-bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO to O) = 0.85395$ . The unpaired electrons created by bond breakage of the double C=O bond requires that two times

the O2p AO magnetic energy  $E_{mog}$  (Eq. (15.60)) be subtracted from the total energy to give  $E_{D}(Group)$  (eV) for C = O.

 $E_T(atom-atom, msp^3.AO)$  of the C=O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is -2.69893~eV which is an energy minimum for the double bond between the pair of  $C2sp^3$  HO electrons of the C atom and the pair of AO electrons of the O atom. It is given as a linear combination of the energy contributions corresponding to a double bond, -1.13379~eV (Eq. (14.247)), and a triple bond, -1.56513~eV (Eq. (14.342)). The triple bond contribution includes the  $C2sp^3$  HO electron of the C-H bond in addition to the pair involved directly in the double bond with O. 10  $E_T(atom-atom, msp^3.AO)$  of the C-C(O)H group is equivalent to that of an alkane, -1.85836~eV, where both energy contributions are given by Eq. (14.513). It is based on the energy match between the  $C2sp^3$  HOs of the aldehyde. In order to match energy between the groups bonded to the C=O, electron-density is shared. Due to the interaction in the transition state between the groups based on the sharing,  $C_{1o}=2C_1$  rather than  $C_{1o}=C_1$  in Eq. (15.52) for the C-C(O)H bond.

The symbols of the functional groups of alkyl aldehydes are given in Table 15.87. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl aldehydes are given in Tables 15.88, 15.89, and 15.90, respectively. The total energy of each alkyl aldehyde given in Table 15.91 was calculated as the sum over the integer multiple of each  $E_D(corrup)$  of Table 15.90 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl aldehydes determined using Eqs. (15.79-15.108) are given in Table 15.92.

Table 15.87. The symbols of functional groups of alkyl aldehydes.

	Groups of any aid
Functional Group	Group Symbol
CH <sub>2</sub> (formaldehyde) group	$C-H(CH_2)$ (i)
CH (aldehyde) group	CH (i)
C=O	C = O(i)
C-C(O)H	C-C(O)H
CH₃ group	$C-H\left(CH_{3}\right)$
CH2 (alkyl) group	$C-H\left(CH_{2}\right)$ (ii)
CH (alkyl)	C-H (ii)
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Charle   C				Т		Γ	$\top$	_	Г-		٦	_
C - H (CH,   C - H (CH,   C - H (ii)   C - C (ii)   C - C (ii)   Group   Gro		C-C(f) Group			2701.7	1 45164	31.963		1.532 (propane)	1,531	(butane)	1.52750
C - H (CH <sub>1</sub> )   C - H (CH <sub>1</sub> )   C - H (ii)   C - C (a)   C - C (b)   C - C (c)   Group   Gro		C-C (e) Group		3 17015	7.101.2	1.45164	1.53635		1.532 (propane)	1.53	COUCEUD	1.52750
C - H (CH, )   C - H (CH, )   Group   Group   Group		C-C (4) Group		2 12/00	416477	1.45744	1.54280		1.532 (propane)	155.1	/augman	1.54616
C - H (CH <sub>1</sub> )   C - H (CH <sub>1</sub> )   C - H (ii)   C - C (a)     Group   Group   Group   Group     1.64920   1.67122   1.67465   2.12499     1.04836   1.05553   1.0561   1.45744     1.10974   1.11713   1.11827   1.45744     C - H propare)   C - H p		C-C(c) Group		2.10705		1.45164	1.53635		1.532 (propane)	(hutene)		1.52750
C - H (CH, )		ر-د (ه) محسل		2.12499		1,45744	1.54280		1.532 (propane)	(butane)	,,,,,,,,	1.34010
C - H (CH <sub>1</sub> )		C-C (a) Group		2.12499		1.45744	1.54280		(propane)	(butane)	1 54616	Diore.
C - H (CH,)   Group   1.64920   1.04856   1.10974   C - H propare)   1.17295		i	l	1.67465		1.03661	1.11827		1.122 (isobutane)		1 20024	
C - H (CH, )   C - H (CH, )   Group   1.64220   1.04836   1.10974   C - H propure)   L   T   C - H propure)   L   T   L   T   T   T   T   T   T   T			dono	1.67122	1,0000	1.03333	1.11713		(C-H propane)	(C-H butane)	1.29569	02150
Parameter   C: - H (CH;) (i)   CH (i)   C = O   C - C(O)H     Parameter   C: - H (CH;) (i)   CH (i)   C = O   C - C(O)H     C  C  C  C  C  C  C  C  C  C  C  C  C		C ~ H (CH,) Group	, ,,,,,	1.04920	1 04856	200.	1,10974	1.107	(C - H propane) 1.117	┱	1.27295	063590
Table   15.88. The geometrical band parameters of alkyl aldehydes and exp     Parameter   C - H (CH <sub>2</sub> ) (1)   CH (1)   C = O     Group   Group   Group     Length   1.10668   1.11827   1.20628     Erp. Bond   1.116   1.128   Gromaldshyde     Changle   Changle   Changle   Changle   Changle     angle     Changle   Changle   Changle   Changle   Changle   Changle     Changle   Changle   Changle   Changle   Changle   Changle     Changle   C	erimental values [1].	C - C(0)H Group	3.04740	4.04/40	1.43087		1.51437		L.515 (acetaldeftyde)		1,46439	0.69887
Table   15.88   The geometrical band parameters of alls	aldehydes and exp	Group	1 29907	200	1,13977		1,20628	1.208	(fornaldshyde) 1,210	(accuaigenyae)	0.62331	0.87737
Table 15.88. The geometrical bands of (a, b)   (1.4010   (a, b)	id parameters of alky	Croup	1,67465		1.05661		1.11827		(acetaldehyde)	, 2006 1	47467·I	0.63095
Table 15.88.   Parameter	The geometrical bon	$C-H\left(CH_{2}\right)(0)$	1.64010		1.04566		1.10668		(fornaldehyde)	1 36264	1.5003.7	0.63756
	Table 15.88.	Varameter	0 (0,)		c. (a°)	Bond	2c' (1)	Exp. Bond	Z	4.5 (a)		0

Table 18.89. The MO to HO intercept geometrical bond parameters of alkyl aldehydes. R.R., R. are H or alkyl groups. Er is E, (anom - anom.axp.).AO).

Bond

	E 012	Ę	F.	E.	E.	Final Total	J		3	1000	ė	,			
		(eV) Bond f	(eV) Bond 2	(eV) Bond 3	(cV) Bond 4	Energy Chr.	(°)	્રે કે	(e.	(cv)	. C	· ©	6° ©	9" (g	, e
אינוסו – מ (מיז) מי	1					(o,				Final	:	;	:	Ē	?
(a) (cu) = (cu) (d)		-1,34946	•	•	•	-152.96515	17716.0	\$1178'O	-16.17521	-14 08414	:				
$-C_{*}H_{3}C_{*}(O)-H_{3}(CH_{3})$ (i)	۲,	-L34946	-0.9291K .	۰	۰	Line Tal.	125.00				77.67	104.28	\$0.18	123314	0.20748
H,C=0	9	1.34946	٥				1/162	0,799an	-17,10440	-{6.91353	64.93	115.05	33.69	1.39345 .	0.33684
$-C_{\kappa}H_{1}C_{\kappa}(H)=0$	0	1.34946		,			1.00000	0,84115	-16,17521		137.27	42.73	1699	0.52193	0.61784
2H,C, -C,(H)(O)	نا	-L34946	A 97918	,	.]		1.00000	0 14115	-16.17521		127.27	42.73	1633	0.52193	0.61784
H,C, -C,(HXO)	ن	-0.92918		,		-153 89434	0.91771	0.79546	-17,10440	-16.91353	135.34	44.66	63.78	0.5740!	0.56576
-C,H, -C,(H)(O)		-0.9291R	¥10400			1373467	177160	0 86359	-13,73493	-15.36407	12.27	£7.701	¥.7	1.693\$\$	0.26301
C-H (CH,)		A10701A		,  ,	•	-153.47405	091771	0.81349	-16.68411	-[6,49325	63.99	10'11	30,58	1.76270	0,33183
C-H (CH.) (ii)	. .	1 10 CO C	20000	3 .	-	-152.34487	0.91771	0.16339	-15.75493	-15.56407	77.49	15.201	41.48	1,2354	0.12703
(ii) (H2) H).	. .			•	0	-153,47406	0.91771	0.81549	-16,63612	-16.49325	68,47	111.53	35.84	1.35436	0.29933
H.C.C.H.C.H.	-	41676:07	-0.9291X	-0.92918	•	-154.40324	17716.0	0.77247	-17,61330	-17.42244	61.10	118.90	31.37	L 4292X	361710
(C'-('a))	. · ·	-0 929   8	c	•	0	152,54417	17716.0	0 86359	-15.73493	-15.56407	63.82	116.18	30.05		areien o
H;C,C,H;CH; -	ن '	\$1626'0-	A1920.0-											Cruco.	0.38100
R-H.C. (H.C R.) HCH =					·	unwi wicci.	1716.0	0.81349	-16 68412	-16,49325	56.41	123.59	25.06	1,90890	0.45117
((c,~(. (p))	ਹ*	1162A G	atege.o.	40.92918	a	-154,40324	17716.0	0.77247	-(7,61330	-17,42244	24.70	12.15		1	
$R = H_1C_*(R - H_2C_*)C_*(R^* - H_3C_*)CH_2 - R_3C_*$	౮	A192918	-0.72457	-0.72457	-0.72457	154 71860	į	275.00						Taylor.	0.51388
init, C, (H.C, - IT) HCH, -	,							esserie.	40×76'.1-	-17.73779	48.21	131.79	21.74	1.95734	0.505.0
(C - C (d))	5	-0.9291x	-0.9291K	-0.92918	0	-154.40324	17716.0	0.77247	-17.61330	-17,42244	48,30	131.70	25.90	1,97162	0.51388
(C'-C'(c))	ڻ	-0.72457	-0,72457	-0,72457	-0.72457	15451399	17716.0	0,76765	17.97866	917.57.71-	50.04	129.96	22.66	SALKS	10,000
$(C-C, (H, C, -K)HCH_1 - (C-C, (H))$	ť	-0,72457	-0.92918	-0.92918	٥	-154.19863	17710.0	0,78155	-17,40869	-17.21783	32.11	22.22	2,5	1 10	
$linK_{s}(R'-H_{s}C_{s})C_{s}(R'-H_{s}C_{s})CH_{s} (C'-C'(R))$	ر.	-0.72457	-0.71457	-0,72457	-0.72457	-134.51399	141160	0.76765	-17,92866	87.07.71	20.02	200		C	6/2/6/0
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( v. (er.)	-72.03287	-35.12015	-111.25473	-30.19634	-107,32728	-70,41425	-35,12015	-28.79214	-28 79714	-20 10112	, m. s.	, ,	-
V, (eV)	26.02344	12.87680	23.87467	9.50874	38.92728	25.78002	12.87680	0 33352	0 21150		0 2225	27.101.72	-23.10112
7 (cV)	21.95990	10,48582	42,82081	7.37432	32,53914	21.06675	10 48587	6 77464	177727	2,31413	7,5552	677/5%	9.37273
V, (eV)	-10.97995	-5.24291	-21.41040	-3.68716	-16.26957	71115 01.	20001.01	2 28 723	0.77404	0.50500	6.77464	6.90500	6.90500
F(.w un) (eV)	-14.63489	-14,63489	٥	-14 63489	-15 56407	16 66 407	20000	70/900	75/25-6-	-3.43230	-3.38732	-3.45250	-3.45250
ΔΕ <sub>11,100</sub> (10.10) (eV)	٥	٥	.2 69801	•	0.000	13.30407	-14,03489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15,35946
15, (m ro) (eV)	-14,63489	-14 63489	208097	277700	3	3	٥	0	0	0	0	0	0
E. (r, w) (cV)	49 66417	-31 K3533	25070.2	14.03409	-13.30407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15,56407	-13,35946	-15.35946
F (atom -atom men! 40) (-V)		CCCCO.IC.	-03.210/4	-31.03334	-67.69451	-49.66493	-31,63533	-31.63537	-31,63537	-31.63535	-31,63537	-31.63535	-31.63535
E land (a.V.)		0	-2.69893	-1.85836	0	o	0	-1.85836	-1.85836	-1,44915	-1.85836	-1.44915	-1.44915
(1013	47,00493	-31.63537	-65.96966	-33,49373	-67,69450	-49.66493	-31,63537	-33,49373	-33.49373	-33.08452	-33.49373	-33.08452	-11 08452
w (10 rau s)	25.2077	24.1759	59.4034	23.3291	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	17955 6	0 55643
( (ak )	16.59214	15,91299	39,10034	15,35563	16.40846	15.97831	15.91299	621159	6.21159	10 19220	621159	t chor y	1000
2, (cv)	-0.25493	-0,24966	-0.40804	-0.25966	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	0.20896	\$1991.0	0.27021	17067-0
C. Line (C.V.)	0.35532	0.35532	0.21077	0.13800	0.35532	0.35532	0.35532	0.12312	0.17978	0.00044	615510	0.10410	-0.75416
E (aV)	-0.07727	-0.07200	20305	126	(Eq. (13.458))	(Eq. (13.458))	(Eq. (13.458))	[2]	[4]	13	[2]	2157	2122
E (cV)	0 14803	E0871 0	17710	200	10,227	-0.14302	-0.07200	-0.10359	-0.07526	-0.15924	-0.10339	-0.10260	-0.10260
Fylory (cV)	49.81948	-31 70737	152110	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E (t. 10 no) (aV)	-14,63489	-14 63480	-(4 63480	33,00439	10776.10-	-49.80996	-31.70737	-33.59732	-33.49373	-33,24376	-33.59732	-33.18712	-33.18712
E 1 111 (eV)	-13.59844	-13.59844	0	00000	-14.03489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489
Entropi (eV)	7,83968	3.47404	7 80660	4 4 146 1	13.39844	-13.59844	-13.59844	0	0	٥	0	0	0
				O. L.	14.2100	7.83016	3.32601	4.32754	4.29921	3,97398	4.17951	3.62128	3.91734

	Relative Error			0.00056	0.00039	0.0000	-0.00022	00000	0.00034	-0.0003R	0.00043	0.00053
	Experimental	Total Bond	Energy (eV)	15.655	28.198	40,345	52.491	52.604	64.682	276.31	101.179	101.29
	Calculated	Total Bond	Energy (cV)	13,646.28	28.18711	40,34481	52.50251	52,60340	64,66021	101 1221	101.1333	101-(038)
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					(Table 15.3.A)		(Table 15.3.A)								>			
(c, H, (O) (i))	2,09132	2.09132	3,5637	-16.390119	×	x	I	0.63008		-	_	6.75	07.02.1			+	116.17	2311 71
AC,C,H RC,(H)=0	2.86175	2,11333	4,7269	-15.75493	_	-14.H2373 C.	_	0.86359	17716.0	6.75	-	0.75	1.06267	0		-	115.32	
0.3'37	2,86175	2.27954	4.3826	-16.68412	n	-13,61806	0	0.81549	0.83395	-	-	-	177.0	,,,,,,		+	1	(acctaidchyde)
Medicion 2HC H	2.11106	2.11106	3,4232	-13.75493	,	=	H	052340	(Fq. (15.114))		. [	-	0.63476	-1,50376		+	125.70	3
							:	Comp.	-	-]	-]	0.75	1.15796	0			108.44	_
ZC,C,C,															15.69		110,49	112 (propane) 113.8 (butane)
		_	_								Ī					1		(Isobuta
M. P., C., H															1569	· · · · · ·	110.49	
ZHC, H	2,09711	11770.2	3,4252	-15,75493		I	×	0.86359	-	1	-	0,75	1.15796	۰		$\vdash$	03 001	┿
ZC.C.						<u> </u>										1		3
H,0,02						<b>†</b>									70.56	-	109.44	
7.7.7.7 70.7.7.				-16 61412		-16.63412									20.56	-	109,44	_
C.	790367	2.91547	4,795B	່:	ม	Ů,	ສ	0.81549	0.81549	-	_	-	0.81549	-1.85836			110,67	110.8
ZC,C, H I∞ C.	2,91347	2.11323	4.1633	-15.55033 C,	•	-(4.12373 C,	-	0.87495	17716.0	6.73	-	67.0	1.04887	0		+	110.76	-
4C,C,H Im C,	2,91547	2.09711	4.1633	-15.53033 C,	3	-14,3333	-	0.87495	171160	0.75	-	67.0	1,04877	0			11137	E
	2.90327	2.90327	4.7958	-15.55013 C <sub>1</sub>	-	-[4,12373 C,	-	0.87495	17716.0	6.73	-	57.0	1.04887	-1.85836	1	+-		+
75.5.75											1				1	$\parallel$		4

KETONES  $(C_n H_{2n} O, n = 1, 2, 3, 4, 5...\infty)$ 

The alkyl ketones,  $C_nH_{2n}O$ , each have a C=O moiety that comprises a functional group. Each of the two single bonds of carbon to the carbonyl carbon atom, C-C(O), is also a functional group. The alkyl portion of the alkyl ketone may comprise at least two terminal 5 methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in ketones are equivalent to those in branched-chain alkanes.

The C=O and C-C(O) groups are solved by hybridizing the 2s and 2p AOs of each C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between 15 the  $C2sp^3$  HO and the O AO or between two  $C2sp^3$  HOs, respectively, to form a MO permits each participating orbital to decrease in radius and energy. In alkyl ketones, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3)=-14.63489~eV$  (Eq. (15.25)) and the O AO has an energy of E(O)=-13.61806~eV. To meet the equipotential condition of the union of the C=O  $H_2$ -20 type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the C=O-bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO~to~O)=0.85395$ . The unpaired electrons created by bond breakage of the double C=O bond requires that two times the O2p AO magnetic energy  $E_{mog}$  (Eq. (15.60)) be subtracted from the total energy to give  $E_D(crosp)$  (eV) for C=O.

As in the case with aldehydes,  $E_T(atom-atom, msp^3.AO)$  of the C=O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is  $-2.69893 \, eV$  which is an energy minimum for the double bond between the pair of  $C2sp^3$  HO electrons of the C atom and the pair of AO electrons of the O atom. It is given as a linear combination of

the energy contributions corresponding to a double bond,  $-1.13379 \, eV$  (Eq. (14.247)), and a triple bond,  $-1.56513 \, eV$  (Eq. (14.342)). The triple bond contribution includes the  $C2sp^3$  HO electron of the C-C(O) bond in addition to the pair involved directly in the double bond with O. Consequently,  $E_T(atom-atom,msp^3.AO)$  of the C-C(O)-bond MO is  $-1.44915 \, eV$ , 5 corresponding to the energy contributions of the two  $C2sp^3$  HOs to the single bond that are equivalent to those of methyl groups,  $-0.72457 \, eV$  (Eq. (14.151)). Since there are two C-C(O) bonds in ketones versus one in aldehydes,  $C_{1o}=C_1$  in Eq. (15.52) for each C-C(O) ketone bond.

The symbols of the functional groups of alkyl ketones are given in Table 15.93. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.55)) parameters of alkyl ketones are given in Tables 15.94, 15.95, and 15.96, respectively. The total energy of each alkyl ketone given in Table 15.97 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.96 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mog}$  that is subtracted from the weighted sum of the  $E_D(Group)$  (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl ketones determined using Eqs. (15.79-15.108) are given in Table 15.98.

Table 15.93. The symbols of functional groups of alkyl ketones.

Functional Group	Group Symbol
C=O .	C = O
C-C(O)	C-C(O)
CH <sub>3</sub> group	$C-H(CH_3)$
CH <sub>2</sub> group	$C-H$ $(CH_2)$
ĊH	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

1301c 13.94	able 13.54. The geometrical bond parameters of an	to parameters of alk	The recommendation of the recommendation of								
Paruneter	0=0	(0)2-2	(C-H (CH)	C-H(CH)	C-H	C-C(a)	(4) 2-2	(e) <i>D-2</i>	C-C (d)	(e) ン-ン	(t)
	Group	Group	Group	Group	Group	Group	Graup	Group .	Group	Group	Group
0 (0)	1,312172	2.04740	1.64920	1.67122	1,67465	2.12499	2.12499	2.10725	2.12499	2.10725	2.10725
c, (a)	1,14550	1,43087	1.04856	1.05553	1.05661	1.45744	1.45744	1,45164	1,45744	1.45164	1,45164
Bond Length 2c' (A)	1,21235	1.51437	1.10974	E1711.1	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1,53635
Exp. Bond Length (A)	1.213 (acetone) 1.219 (2-bulanone)	1.520 (acelone) 1.518 (2-butanone)	1,107 (C-H propane) 1,117 (C-H butane)	1.107 (C-H propane) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1,532 (propunc) 1,531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
h.c (a,)	0.64002	1.46439	1.27295	1.29569	1.29924	1,54616	1.54616	1.52750	1.54616	1.52750	1.52750
а	0.87298	0.69887	0.63580	0.63159	0.63095	0,68600	00989'0	0.68888	0.68600	0.68888	0.68888

Table 15.95. The MO to HO intercept geometrical hond parameters of alkyl ketones.	rical bond	parameters of al.		R, R', R" are H or alkyl groups.	alkyl groups.	$E_{r}$ is $E_{r}(atom$	$E_r$ is $E_r(atom - atom, msp^*, AO)$	o) '								
Bond	Atom	. E.	E.	Er	<i>E</i> <sub>7</sub>	Final Total Fnerry	<u>, 1</u>	7	Ermine (e.V)	$E(C2sp^3)$	ie	9	i o	'p'	, d,	
		(ev) Bond i	(ev) Bond 2	(eV) Bond 3	(eV) Bond 4	(22p)	(aº)	(%)	Final	(eV) Final	(.)	(°)	(。)	(a,)	(°)	
$R'C_*H_1(RC_*H_1)C_*=0$	0	-1,34946	0	0	0		1.00000	0.84115	16.17521		136.09	43.91	65.72	0,53955	0.60595	
$R'C_{*}H_{2}(RC_{*}H_{3})C_{*}=0$	.; :	-1.34946	-0.72458	-0.72458	0	-15441430	17115.0	0,77199	-17.62437	-17,43350	133.02	46.98	98.19	87819.0	0.52672	
H,C, -C, (O)(R')	ئن	-0.72458	0	0	0	-152,34026	17716.0	0.87495	-15,55033	-1535946	73.62	106.38	34.98	1,67762	0.246675	
RH,C, -H,C, -C, (O)(R')	ئ	-0.72458	-0.92918	0	0	-153.26945	17710	0.82562	-16,47951	-16.28865	67.40	112.60	31.36	1,74821	0.31734	
C-H (CH <sub>3</sub> )		-0.92918	0	0	0	152,54487	17719.0	0.86359	-15.75493	-15,56407	77,49	102.51	41.48	1.23564	0.18708	
C-H (CH <sub>1</sub> )	ر.	-0.92918	-0.92918	0	0	901/1531-	17716.0	0.81549	-15,68412	-16.49325	68.47	111.53	35.84	1,35486	0.29933	
C - H (CH)	٠.,	-0.92918	-0.92915	21626'0-	0	- [ \$4,40324	17718.0	0.772A7	-17.61330	17,42344	61.10	118.90	11,37	1.42988	0.37326	
H,C,C,H,CH, - (C'-C'(a))	Ú,	-0.92918	0	0	0	-152,54487	17716.0	0.86359	-15.75493	-15,56407	63.82	116.18	30.08	1.83879	0,38106	
H,C,C,H,CH, -	τ,	-0.92918	-0.92918	0.	U	-153.47406	171180	0.81549	-15.68412	.16.49325	56.41	123.59	26.06	06806'1	0.45117	
$R = H_2(f, G_1(H_2G_2 - R))H(H_2 - G_2(G_2))$	c,	81676'0-	-0.92918	-0.92918	o	-154.40324	122160	0.77247	-17.61330	-17,42244	48.30	131.70	21,90	1.97162	0.51388	
$R = H_2C_s(R^2 - H_2C_s)C_k(R^2 - H_2C_s)CH_3 - (C^2 - C^2)C_3$	ن	-0.92918	-0.72457	-0.72457	-0.72457	-154.71860	17710.0	0.75889	-17.92866 .	-17.73779	48.21	131,79	21.74	1.95734	0.50570	
$hoC_{*}C_{*}(H_{*}C_{*}-R^{*})HCH_{2}-(C^{*}-C^{*}(d))$	C.	#1626'0-	-0.92918	\$162 <u>6</u> .0-	0	-154 40324	12216.0	0.77247	-17.61330	-17,42244	48.30	131.70	21.90	1,97162	0.51388	
$ler(C_{n}(R^{-} + H_{n}C_{n})C_{n}(R^{-} + H_{n}C_{n})C_{n}H_{n} - H_{n}C_{n})C_{n}H_{n} - C_{n}(R^{-} + H$	۲.	-0.72457	-0.72437	-0.72457	-0.72457	-134.51399	17716.0	0.76765	-17.92866	•17.73.	\$0.04	129.96	22.66	1.94462	0.49298	
ופחנ", ("ב", "ב") אכיא" – וני" – נ' (ח"ב", – א') אכיא" –	Ċ,	20,72457	-0.92918	-0.92918	გ	-154.19863	17716.0	0.78155	-17.40869	817.12.71.	52.78	17.72	24.04	D+26-1	0.47279	
$l(C-C'(R^2-H_2C_a)C_b(R^2-H_2C_a)CH_2 - C_b(R^2-H_2C_a)CH_3 - C_$	ť	-0.72457	-0,72457	-0.72457	-0.7257	46515 PS1-	17710	6,76765	-17.92866	-17.73779	50.04	129.96	22.66	1,94462	0.49298	•

tacion in the control of the control		Dildicipal groups of diagraphics.			22 0	(1)	(F) (F)	(1)	(1)	12/ 17-1	() () - J
	Group	Group	Group	Group	Grand	Group	Group	Group	Group	Group	Group
п	2	_	3	2	-	-	_	-	-	1	-
'u	٥	0	2	1	0	0	٥	0	0	0	0
'u	0	0	0	0	o	0	0	0	0	0	0
	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
ະົ	-	-	-	-	-	1	-	-		-	-
9	-	-	-	-	-	-	1	-	1	1	1
ď	0.85395	111160	12216'0	17716.0	17716.0	0.91771	174160	17716.0	177160	17716.0	17716.0
6,3	2	0	0	1	-	0	0	0	]	1	0
3	4	2	-	-	-	2	2	2	2	2	2
6	0	٥	3	2	-	0	o	٥	٥	0	o
	9.5	1	0.75	0.75	0.75	5.0	. 0.5	0.5	0.5	5.0	6.5
ر"	_	-	-		-	-	1	1	1	1	-
V, (cV)	-109.17602	-30.19634	-107.32728	-70,41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	21101.62-	-29.10112
V, (aV)	23,75521	9,50874	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	6,37273	9.37273
T (cV)	41.60126	7,37432	32.53914	21.06675	10.48582	6.77464	6.77464	6,90500	6.77464	6.90500	6.90500
V_ (eV)	-20.80063	-3.68716	1569231-	-10,53337	-5.24291	-3.38732	-3,38732	-3.45250	-3.38732	-3,45250	-3.45250
E(no not (eV)	0	-14,63489	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15,56407	-1535946	-15.35946
ΔΕ <sub>π,110</sub> (.r. n) (eV)	-1,34946	. 0	0	0	0	0	0	D	0	0	0
$E_T(win)$ (eV)	1.34946	-14.63489	-15.56407	-15.56407	-14,63489	-15.56407	-15.56407	-15.35946	-15,56407	-15.35946	-15,35946
Er(n,w) (cV)	14047 69-	-31.63534	-67.69451	-49,66493	-31.63533	-31.63537	-31,63537	-31.63535	-31.63537	-31,63535	-31.63535
$F_{\tau}(alom - alom, msp^2, AO)$ (cV)	-2.69893	-1,44915	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1,44915	-1.44915
E. (12) (cV)	99696'59-	-33.08452	-67.69450	-49,66493	-31,63537	-33,49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
(101) rod/s)	\$7.0928	16.4962	24.9286	24,2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
(K (vV)	37,57947	10.85807	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
(Na) "2	-0.40003	-0.21568	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Ein (aV)	0.21462	0.(4655	0.35532 (Eq. (13.458))	0,35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978	0.09944	0.12312 [2]	0,12312 [2]	0.12312 [2]
('¢')	-0.29272	-0.14240	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
(dV)	0,11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
F. (imm) (cV)	-66.55510	-33.22692	-67.92207	-49.80996	-31,70737	-33.59732	-33,49373	-33.24376	-33.59732	-33.18712	-33.18712
( / a) ( or or 1) ( an)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14,63489	-14,63489	-14.63489
Burne (n. 10 10) (eV)	D	0	-13,59844	-13.59844	-13,59844	0	0	0	0	0	0
E, (im) (aV)	7.78672	3.95714	12.49186	7.83016	132601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

72.50

847495

-14.82575

-15.55033 C,

2.90327

Table 15.97. The rotal band energies of alkyl ketones calculated using the functional group composition and the energies of Table 15.96 compared to the experimental values [3]. The magnetic energy E<sub>me</sub> that is subtracted from the weighted sun of the E<sub>0</sub> (cm.) (ct/) values based on composition is given by (15.57).

			,											<del>, .</del>	, -	r			_
Relative Error	-0.00031 -0.00005 -0.00005 -0.00005 -0.00005	0.0001 0.00031 0.00031 0.00032	0.00007 -0.00093 -0.00049 0.00001 0.00027		Exp. θ		116.0 (acctone)	113.5 (2-butanaone)	121.9 (2-butanagne)	107 (propans)	112 (propane) 113.8 (butane) 110.8 (izobutane)	111.0 (butane) 111.4 (subutane)	108.5 (acetons)			(10.1 (sobutane)		111.4 (isobutane)	
Experimental Total Bond From (eV)	40.672 84.997 64.997 65.036	71.13 71.17 71.17 78.18 78.18	89.458 89.434 (01.660 113.632 113.675		हुं <u>C</u>		115.77	113.71	122.07	101.44	110.49	110.49	109.50	109.44	109.44	110.67	110.76	111.27	1
					0° ©														
Calculated Total Bond Formy (eV)	65.00012 65.00012 65.00012 65.00012	77.15782 77.25871 77.29437 89.31552	89.45202 89.51730 101.71061 113.63092 113.63092		e_ ©														
	1				ø, 💽						15.99	69.51		70.56	70.56				
C-C() E.	00000		,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		E, (eV)		-1.85836	-1.85836	-1.44915	0	•		0			-1.85836	0	0	
1				118p³.40).	٧		0.B1549	0.81549	0.86445	1.15796			1.15796			0.81549	1.04117	1.04887	1
(a) 2-2 (e)	00000		00000	<i>atom – atom</i> .	u-	1	-	-	-	0.75			0.75			 	st.o	0.75	1
C-C(d)	00000			. Er is Er (	ΰ		_	_	-	-			-			-	-	-	t
(c) -C	••••	000000	~~~~	le were used	כי		<b>-</b>	1	-	1			-			-	0.75	0,75	1
(q) 2-2	000000	000000	2 <del>4</del> 4 0 0 w	preceding an	C, Aten 3		0.81549	0.81549	0.85395 (Eq. (15.114))	•			-			0.81549	17719,0	17716.0	
C-C (a)	0 – 2 11 0 m		-00000	neters from the	Cy Abm I		0.81549	0.81549	0.87495	0.86359			0.86359			0,81549	0.87495	0.87495	
Ð	000-0	00-000	00000	Table 15.98. The bond angle parameters of alkyl ketones and experimental values [1]. In the calculation of $ heta_*$ , the parameters from the preceding angle were used. E, is E <sub>f</sub> (atom - atom, mrp³ AO)	Atom 2 Hybridization Designation	(Table 15.3.A)	25	25	o	Ħ		i 	н			æ	-	_	
GF,	0-1101	1 m 0 4 4 -	- 0 0 0 0 n	n the calculat	F.Carterior	-16 68412	C,	-16.68412 C.	-13.61806	=			н			-16.68412 C,	-14.82575 C,	-14.82375 C,	
CH,		14440	*****	ntal values [1]. It	Atom I Hybridizarion Designation	(Table 15.3.A)	22	25	s	7	ļ		7			52	\$	~	
Group	~~~~	14444	* ~ ~ ~ ~ ~	and experime	Eradonia Asom I	-16.68412	ڻ	-16.58412 C.	15,55033	-15.75493			-(5,75493			-16.68412 C.A	-15.55033 C,	-15.55033 C,	
C=O Group				kyl ketones	2c' Terreinal Aleses ( a, )		4.8477	4.8374	4.5166	3,4252			3.4252			4.7958	4,1633	4.1633	
			2	neters of al	(a, )		2.86175	1.86175	2,79100	2.11106			1.09711			2,91547	2.11323	2.09711	
Name Name	Acatone -Buranone -Pentanone -Pentanone -Methyl-2-buranone -Heramone	3-Hexanone 2-Methyl-3-pentanone 33-Oimeliyl-2-butanone 4-Hoptanone 4-Hoptanone 2-Dimental	2.4-Dimethyl-3-pentanone 12.4-Trimethyl-3-pentanone 2.Nonanone 5-Novanone 5-Novanone 1.6-Dimethyl-4-hexanone	d angle paran	2c' bed ( (a,)		2.86175	2.91547	2,86175	2,11106			2.09711			291547	291547	2.91547	
ila ila				5.98. The bon	Atoms of Asyle		לנ'נ'(ס)נ'	(o)':2'2'	0,2,22	ZHC,"H	לכ"כ"כ"	ZC,C,H	Methit ZHC"H	۲C,C,C,	CC,C,H	رد'ر'ر' ه ر.'	ДС,С,Н In C,	,7.2,74 ±.0,74	1000
Formula	Q Q Q Q Q Q Q Q Q Q Q Q Q Q Q Q Q Q Q	333333	100000	Table	<		Ø	×							1				

## CARBOXYLIC ACIDS $(C_n H_{2n} O_2, n = 1, 2, 3, 4, 5...\infty)$

The alkyl carboxylic acids,  $C_nH_{2n}O_2$ , comprise a C=O functional group, and the single bond of carbon to the carbonyl carbon atom, C-C(O), is also a functional group. Formic acid has a HC=O moiety that comprises a more stable C=O functional group and a CH functional group. All carboxylic acids further comprise a C-OH moiety that comprises C-O and OH functional groups. The alkyl portion of the alkyl carboxylic acid may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acids are equivalent to those in branched-chain alkanes.

The CH functional group was solved in the Hydrogen Carbide (CH) section except that the energy of the C-H MO is matched to the carbon-atom contribution to  $\Delta E_{H,MO}$  (AOIHO) and  $E_T$  ( $atom-atom, msp^3.AO$ ) of the C-O group. The alkyl carboxylic acid C=O and C-C(O) groups are equivalent to those given in the Aldehydes section except that  $\overline{E}_{Kuh}$  is that of a carboxylic acid. The formic acid C=O group is solved equivalently to that of the alkyl carboxylic acid group, except that  $\Delta E_{H_1MO}$  (AOIHO) and  $E_T$  ( $atom-atom, msp^3.AO$ ) correspond to a 25% increase in the donation of charge density from the orbitals of the atoms to the C=O MO due to the presence of a H bound to the carbonyl carbon. Also,  $\overline{E}_{Kvib}$  is that corresponding to formic acid. The C-O and OH groups are equivalent to those of alkyl alcohols given in the corresponding section except that the energy of the C-O MO is matched to that of the C=O group and  $\overline{E}_{Kvib}$  is that of a carboxylic acid.  $\Delta E_{H_1MO}$  (AOIHO) of the C-O group is equal to  $E_T$  ( $atom-atom, msp^3.AO$ ) of the alkyl C=O group in order to match the energies of the corresponding MOs.

As in the case with aldehydes and ketones,  $E_T(atom-atom, msp^3.AO)$  of the C=O-bond MO in Eq. (15.52) of alky carboxylic acids due to the charge donation from the C and O

atoms to the MO is  $-2.69893 \ eV$  which is an energy minimum for the double bond between the pair of  $C2sp^3$  HO electrons of the C atom and the pair of AO electrons of the carbonyl O atom. It is given as a linear combination of the energy contributions corresponding to a double bond,  $-1.13379 \ eV$  (Eq. (14.247)), and a triple bond,  $-1.56513 \ eV$  (Eq. (14.342)). The triple bond contribution includes the energy match of the carbonyl  $C2sp^3$  HO electron with the O of the C-O-bond MO in addition to the pair involved directly in the double bond with the carbonyl O.

 $E_T(atom-atom,msp^3.AO)$  of the formic acid C=O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is  $-3.58557\,eV$ . This is also an energy minimum for the double bond between the pair of  $C2sp^3$  HO electrons of the C atom and the pair of AO electrons of the carbonyl O atom. It is given as a linear combination of the energy contributions corresponding to a triple bond,  $-1.56513\,eV$  (Eq. (14.342)), and a quadruple bond,  $-2.02043\,eV$  (Eqs. (15.18-15.21) with s=4)) where the bond order components are increased by an integer over that of alkyl carboxylic acids due to the presence of a H bound to the carbonyl carbon.

 $E_T(atom-atom, msp^3.AO)$  of the carboxylic acid C-C(O) group is equivalent to that of alkanes and aldehydes, -1.85836~eV, where both energy contributions are given by Eq. (14.513). It is based on the energy match between the  $C2sp^3$  HOs of the carboxylic acid. As in the case of aldehydes,  $C_{1o}=2C_1$  in Eq. (15.52).

 $E_T(atom-atom,msp^3.AO)$  of the carboxylic acid C-O group is equivalent to that of alkyl alcohols,  $-1.85836\,eV$ . It is based on the energy match between the O AO and the  $C2sp^3$  HO of a methylene group (the maximum hybridization for a single bond) where both energy contributions are given by Eq. (14.513).  $E_T(atom-atom,msp^3.AO)$  of the C-O group matches that of the C-C(O) group.

The symbols of the functional groups of alkyl carboxylic acids are given in Table 15.99. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acids are given in Tables 15.100, 15.101, and 15.102, respectively. The total energy of each alkyl carboxylic acid given in Table 15.103 was calculated as the sum over the integer multiple of each  $E_D$  (comp) of Table 15.102 corresponding to functional-group composition of the molecule. For each set of unpaired

electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mog}$  that is subtracted from the weighted sum of the  $E_D(G^{mup})$  (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl carboxylic acids determined using Eqs. (15.79-15.108) are given in Table 15.104.

Table 15.99. The symbols of functional groups of alkyl carboxylic acids.

Functional Group	Group Symbol
CH (formic acid) group	C-H (i)
C-C(O)	C-C(O)
C=O (formic acid)	C = O (i)
C=O (alkyl carboxylic acid)	C = O (ii)
(O)C-O	C-O
OH group	OH
CH₃ group	$C-H\left(CH_{3}\right)$
CH <sub>2</sub> group	$C-H$ $(CH_2)$
CH (alkyl) group	C-H (ii)
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

Table   5,   100   The recomenical bond parameters of all by carboxylle acids and experimental values   11   11   11   11   11   11   11		$\begin{array}{c cccc} OH & C-H \left( CH_{+} \right) & C-H \left( CH_{+} \right) & C-H \left( ii \right) & C-C \left( i \right) \\ Group & Group & Group & Group \\ \end{array}$		0.91808 1.04856 1.05553 1.05661 1.45744		(Gamic acid) (Carlic acid) (C-H blume) (Music) (C-H blume) (Music) (Mu	1,29569 1,29924	0,72615 0,63540 0,63159 0,63095 0,68600	carboxylle scids. R, H, $R^n$ are H or alkyl groups. E, is $\mathcal{E}_{\ell}$ (atom-atom, mxp) $AO$ ).	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0 (1150) 1150) 0 (1150) 0 (1150)	SCIOI CONSCEIT GENERA DENNOI U	MATER SPACETI. CTPLETT: DESTE TITLE SPECELY. O	0 1.00000 0.00359 1.5.73423 101.32	0.194 17213. 1.18.03354 178.02. 0.196.	01.761 (\$21133). 1731.00 00000.)	12361 2055C11- 2115C11- 0551TD 111100 2011(2011- 0	0 (1921) 144115 - 14617321 0 137.27	TALES 1744 TIL RECEORS. TREETO 177100 SELECTESI. O	08.99 SEXT.1. THE.T. WELL ITTIES STILLED IN	82.62 ITEM TI. 88880A. TABLE D. 19790 SECTIBEL O
150   150	nerimental values [1].	(ii) C=0	-	-			-	H	boxylic acids. R.H., R" are	(eV) Bond 3		_	-	-			_		-	_	1946 - A.9291x
(1.0970) (1.	omenical bond nemapers of ally carboxylic acids and expe	H (i) $C - C(0)$ $C = 0$ (i) $C = 0$ Group	2,04740 1,290700	1,43087 1,13613	1,51437 1,20243	1,520 1,502 3d) (scetic acid) (formic acid)	1,46439 0,61267	0,6987 0.88018	Table 15.101. The MO to HO intercept geometrical bond parameters of alkyl carb	(eV) Bond i	402291x	41929134	-19291x	4192918	A192974	HE271-	KT297.1-	94646.1-	-1,34946	47.292.1.	RH.C C. (0) 0H

			•		L.	LINE TOTAL			E	ارت س) يا	.6	6	9	6	ď
		r :	F :	f :	į	Energy	ì	3 (	ş	1	. 3	- 3	73	- (	7
		Bond !	Bond 2	Bond 3	Bond 4	7.5	(ö)	(°)	Final	Y'ev	5	Ξ	E	(ø)	<u>6</u> ,
H-01	2	A9291x	=	e	c		1.00000	0.86359	.15.75493		115.00	16.19	61.13	0.53182	0.35525
HO-1	0	41 020194	9	u	·		I onnari	O PACTUD	-15.75493		101.01	78.68	48.58	1,14765	0 16953
но0H	U	RIGIGIY	-f.7927#	c	e.	-154.33765	14160	0.77.516	£77.8£71.	.17 356.85	P6'156	90.94	47.64	1.26386	620300
C. (0)-0H	0	4192318	c	5	6		1.0000	0.86339	.15.73493		101.32	73 GB	48.58	1,14765	0.16950
C, (0) - OH	ن	×1626℃	.1,349.4r	\$1626 Cr	¢	-154.82352	17716.0	0.75447	.(R0338A	-1784271	91.96	13 65	61,90	1,29138	0.02.578
H)=0	0	HE297.1-	c	0	c		(, nongo	0.81871	.  6.61\$53		137.10	42.50	65.45	0.53635	0.59978
H)=0	ij	жт.297.1-	A9291K	ç	. с	-15433766	17716,0	0.77536	47.54772	17,35485	135.24	91.14	2019	0.58%!	0.55053
(C, (OH) = O	0	-1.34946	e	С	c		1,00000	\$11780	- 46 17521		137.27	42.73	(631	0.52193	061724
C,(OH)=O	ن.	1,34946	4192918	X162617	c	52(18.25)·	141160	0.73447	-18 03358	-17 84271	133.47	46.53	61.46	0.62073	A\$1905
ною.	-	4T.295.1.	ньтеп-	е	в.	.154,33766	14116.0	0.775.W	11.54712	-(7,15045	69.89	110.11	36.00	1,30373	0.26662
-C,(n)nH	ن	40.92918	71.3194ñ	A19291X	c	154 17353	0.01771	0.754.7	.18.03358	1753.871-	\$6.25	123.75	15.55	1.65002	041915
но(о)	ئ	4192918	c	0	o	15254487	177100	0.86359	16152'51	-15.56407	12.27	107,73	34.17	1.69388	0.26301
H,C, -C,(0)DH	٠,	-0.0191x	#1626 tJ.	c	=	153.47405	17716.0	081349	11863811	-16,49,125	63.09	114.01	30.58	1.76270	0.33183
(r.n.)	ن	*1656 O-	c	e	0	TALL SAUNT	0.91771	0,86359	.13.75493	15.56417	77,49	102.5[	41.48	1.27564	0.18703
(c'';)	j	40,92918	#1676 O*	0	0	SUTLT'EST-	וענוטש	6421411	-16.0412	.16 49325	68.57	11.33	35.84	1.35486	0.29913
(c.H) (ti)	٠٠	#1620.0-	41629.0	A 91918	.e	154,40324	17716.0	נאנונט	-17 61330	-17.43344	61,10	118.50	31.37	1.42.0%	0.37326
,H;(H; - (n))	٠,٠	-0 9291x	o	0	0	MULTEL SI-	177100	1186359	-15.73493	-15.56407	63.63	116.18	30.08	1,85879	0.38176
, H; ('H; ~ (a)		-a,9226#	#1620°O	G	0	901217811	12216	aris49	-16/04/12	-16 19323	17'95	67(1)	36.06	00805"	0.45117
(C,C,(H,C,-K)MCH,-		#16t@u-	#1929.th	#1626.0-	ų.	124,40374	177100	ቤጠኔባ	-17,61330	-17.4224	48.30	131.70	21.90	1.97162	0.51388
$C_{*}(R^{-}H_{*}C_{*})C_{*}(R^{-}H_{*}C_{*})C_{*}H_{*}-$ (c)	٤,	#16261P	47.74	40,72457	0.72457	-(34,718/0	17116-0	0.75889	93826'21-	91727.71-	48.31	131.79	21.74	1.95734	0.50570
$\lambda(H_1C_1-R^2)H(H_1-R_2)$	ڻ	#10550-0-	ж1626 а-	#1620/O	a	15(0)*161-	17116-0	14575.0	מנצוש'נו-	יונני'נוי	48,10	131.70	21.90	1.97162	0.51388
(e)	ڻ	13127.11-	1317. O.	40.72487	1215.17.0.	66415751-	17719.0	0,74765	-17.93KG	91717 71.	\$004	129.96	22 66	1.94402	0.49298
$(H_{\epsilon}C_{\epsilon}-R^{*})HCH_{\epsilon}-$	رڙ	isticur	жисть	4)1251K	ė	(3461'151+	12216.0	0.78[55	(eNor't)	54(15.7)	\$2.78	12.22	мм	1.92413	0 47279
"-H;C,)C,("-H;C,)CH;-	u d	RUCTIL	rstct,n.	13157	-0,72457	.154.51.99	177100	0.76763	+17.928c4	פוננע נו-	75.55	129.96	997.	CONTS'1	0.4723K

Parameters () () () () () ()	() #)	(c)-2	(0) ()*.3	.1	0-0	HO	CH.	('H'.	(I) H-J	(a) C-C	(Q) J-2	(e) .72	(P) .)-;	ن-ر (٥)	(J) (J-)
	Стоир	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
4	-	-	2	2	-		ſ	2	-	-	-	-		1	-
7	۰	٥	0	0	•	٥	2	-	0	0	0	0	0	٥	0
ž.	٥	0	0	0	0	0	0	0	0	0	0	0	0	0	0
į.	0.75	0.5	50	5.0	0.5	0.75	0.75	0.75	0.75	2.0	0.5	6.5	0,5	0.5	20
ئ	-	-	-	-	-	-	-	-	-	-	-	-	-		-
6,	-	-	-	-	-	0.75	_	-	-	-	-	-	-	-	1
5	17716.0	17716.0	0.85395	0.85395	0.85395	-	14416.0	0.91771	177160	124160	14416.0	12216'0	17716.0	17716.0	17710.0
ซ	۰	٥	3	2	0	-	0	-		0	0	0	-	-	0
۵,	-	2	4	4	2	-	1	1	-	2	2	7	2	2	2
6	-	0	0	0	0	_	3	2	-	0	0	0	0	0	0
ئن	0.75	-	0.5	0.5	0.5	0.75	0.75	6,75	0.75	0,5	0.5	6.5	0.5	5.0	50
Ċ.	-	-	-	-	-	-	_	-	-	-			-	-	-
(4)	-36.74167	-30.19634	112,61934	-111.23473	-35.08483	-40.92709	\$2728,701.	-70.41425	-35.12015	-28.79214	-28.79214	21101.62-	-28.79214	-29.10112	-29.10112
V, (cF)	13.11890	9.50874	73.95107	23.87467	10.32968	14.81983	38.92728	25.78002	12.87680	9,33352	232226	61272.9	933352	5,772,0	9,37273
T (eP)	11,38634	7.17432	43.62389	42,82081	10,11150	16.18567	32.53914	21.06675	10,48582	6.77454	6.77464	6.90500	6.77454	6.90500	6.90500
1', (aV)	-5.69317	-3.58716	50118,12-	-21.41040	-5.05575	-8.09284	1626957	-10.53337	-5.24291	3.38732	-3.38732	-3.45250	-3,38732	-3,45250	-3.45250
Elminol (el')	.14,63489	-14.63489	0	0	-14,63489	-13.6181	-15.56407	-15.56407	-14,63489	-15.56407	-15.56407	-15.35946	-15.56407	-1535946	-15.35946
DEntrollion my (cV)	.0.92918	0	-3.58557	-2,69893	-2.69893	0	0	0	0	0	•	0	0	0	٥
E, Liornal (cl')	-13.70571	-14.63489	3,58557	2,69893	-11.93596	-13.6181	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-1535946	-15.56407	-15,35946	-15,35946
Erinano) (el')	-31,63530	-31.63534	57075.63-	-63.27074	131,63541	-31.63247	18469.79-	-49.66493	31,63533	-31.63537	-31.63537	-31,63535	-31.63537	-31,63535	-31.63535
E, (otom - atom, msp' A() (cV)	۰	-1.85836	-3.58557	-2.69893	-1.85836	0	0	c	0	-1,85836	988831-	-1,44915	-1,85836	-1.44915	-1,44915
Ertical (cf.)	-31.63537	-33,49373	-66.85630	-65.96966	-33.49373	-31,63537	-67.69450	-49.66493	-31,63537	-33.49373	-33.49373	-33.08452	-33,49373	-33,08452	-33.08452
(10° rod 1.8)	26.0575	1925.62	1856'09	59.4034	24,3637	44.1776	24,9286	24.2751	24.1759	9.43699	9.43699	15.4845	9,43699	9,55643	9.55643
E. (el')	17.15150	15.35563	40,12366	39,10034	16.03660	29,07844	16,40846	15.97831	15.917.89	6.21159	621129	10.19220	621129	6.29021	6.29021
E, (4))	-0.25920	-0.25966	-0.41891	-0.40804	-0.26535	-0.33749	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Ena (cV)	0.35532 (Fa (13.458))	0.10502	(30)	121077	0.14010	0.46311	0.35532	0.35532 (Fo. (13.458))	0.35332 (Fn (13 458))	0.12312	0.17978	15]	0.12312	0.12512 ICI	0.12312
E_ (eV)	-0.08153	-0.20715	-0.30918	-0,30266	-0.19530	-0.10594	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	09:00:0
F (eV)	10351.0	0.14803	0.11441	0.11441	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0,14803	0.14803	0.14803	0,14803	0.14803
Estomal (el')	-31.71690	-33.70088	-67,47466	-66.57498	-33.68903	-31.74130	-67,92207	49.80996	-31.70737	-33.59732	-33,49373	-33.24376	-33.59732	-33.18712	-33.18712
Errenth, so int (et)	-14.63489	-14.63489	-14 63489	-14.63489	-14.63489	-13.6181	-14.63489	-14.63489	-14.63489	.14.63489	-14,63480	-14,63489	-14.63489	-14.63489	-14,63489
Franch by at 18th (cf.)	-13.59844	0	0	0	0	-13.50844	-13.59844	-13.59844	-13,59444	0	0	0	0	0	0
Entone (c)	3.48357	4,43110	8.70628	7.80660	4,41925	4.41035	12,49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.103. The total bond energies of alkyl carboxylic acids calculated using the functional group composition and the energies of Table 15.102 compared to the experimental values [3]. The magnetic energy E\_\_\_ that is subtracted from the weighted sum of the E\_p(n\_\_) (eP) values based on composition is given by (15.51).

| Formula | Name | C - H (i) C - C(i) C = O(i) 
(e) (--( (P) (-C (p) C-C (c) (3)-1 (1) (1) 3 3 C=() ()

Ep. ()	(formic setial)		(Armic axid)	106.3 (Remie acid)	126.6	110.6		(07 repute)	(propage) (13.8 (Procance) 110.8 (Procance) 110.8 (Procance)	(111.0 (mt.ms)	108.5			110 t (sohutzne)		111.4 (pobumb)	[[[,4 (achtume)	
	13.52 t	110.76	13.44 (ft)	107.71 (Re	07.521	109.63	126.03	108.44	69.61	67:01	02.001	┞	2		×e	$\vdash$	<b>-</b>	B
(C.	- F	=	3	ō	1 2	₽	2	≊	=	2	1 €	109.44	109.44	110,67	110.76	111.20	fti.27	107.50
P. C.	-	-	-	_	-	-	-	$\vdash$			$\vdash$	$\vdash$	-	_	-	-		L
e ()	_	-	_	-	-	-		-		-	$\vdash$	*   *	70.56		<del> </del>	-		8
-	-	-	_	-	-	-	-	-	2.6	69.51	├	ş	ğ		_	-	_	22.50
₹. §	6		-1,44915		-1.63376	1,44915	1,44915	c			e			-1.45836	c	•	9585870	
V	0.976.0	0 97/000	0,84113	0.91771	0.83472	0.85877	0.8337	1.157%			1.13796			0.81540	1.04R87	1.Dares7	1,04887	
ů.	0.75	6.75	-	6.19	-	-	-	6.75			0.75			-	27.0	67.0	6.75	
೮	-	-	-	-	-	-	-	-			-			-	-	-	-	
t.	a.rs	0.73	-	87.0	-	-	-	-			-			-	678	67.3	£1.0	
.5. years	045395 (Eq.(!5.114))	0.83395 (Eq. (15.11.1))	0 86359	Q91771	0.85395 (Eq. (15.114))	043395 (Fq.(15.114))	016339	-			-			0.81549	17116.0	0.91711	11116.0	
ر. الله	674795	0.87495	LRIE		041540	บานเก	511740	n.mct50			0.000			0.81549	0.87.49.5	0.87495	0 87405	
Aken 2 Hybridizaden Basignstien (Tatte 15.1A)	0	c	,	-	0	υ	,	н			=			RT.		-	1	
Property of the same of the sa	13.619.06	-13.61706	-15.73495	-14,72575	-13,61m6	יוז עו מטן	£0157.2.1.	π			Ξ.			.10,0MIZ	, casts 7	-14,0273 .0.	-14.R2575 (*,	
Auru 1 Fishtdibaton Basigmiku (Table 15.3A)	\$	\$	t		7	1	73				7			я	\$	~	\$	
E. North	-15.55ms f"	13.55m3	-16.6(1833 O_	-14XB73	-IEGHII	48.75403	-16.17231 O	-15,75493			18.73493			-Infortiz	.15.55033 C,	.15 55033 C.	-13.55ms	
30, Tomper No. (0,)	3 1916	31301.1	4,3243	3,640\$	4,5036	17077	43818	3 4252			14252			4,7958	4.1633	4,1633	4.7958	
(a,)	taget	וטיטיז	זערנוו	ויאפעוע	127%	ועמוו	16431	2111156			HEOT			2.91547	211323	111602	1,900,07	
2c' ('a')	MAGUUT	LOKSON	12727	זעמוו	2,46175	2.95(1)5	2.27054	2.11176			1112011			2,91547	1,91547	2,91547	2.50317	
-Verse of Jugits	CH (i): C=0 (i)	(CH (I))	10.707	CH (0; C=0 (0))	d'C.O.	*0´.'\	40,0,0°	H'.MO	מנ"נ"נ".	H'J',17	H":H7	'J',J',J'	A'.C,H	#.C.,	ZC,C,H ~ C,	4.7.H 4.7.H	יים נ" קניניני	4C,C,C,

Toble (5.104. The bond angle parameters of alkyl carbonylic seids and experimental values [1] In the calculation of 0, the parameters from the preceding angle were used. E, is E, (atom - mom, may). A(0)

## CARBOXYLIC ACID ESTERS $(C_n H_{2n} O_2, n = 1, 2, 3, 4, 5...\infty)$

The alkyl carboxylic acid esters,  $C_n H_{2n} O_2$ , comprise a C = O functional group, and the single bond of carbon to the carbonyl carbon atom, C-C(O), is also a functional group. Formic acid ester has a HC = O moiety that comprises a more stable C = O functional group 5 and a CH functional group. All carboxylic acid esters further comprise a COR moiety that comprises a C-O functional group and three types of O-R functional groups, one for R comprising methyl, one for R comprising an alkyl ester group of a formate, and one for R comprising an alkyl ester group of an alkyl carboxylate. The alkyl portion of the alkyl carboxylic acid ester may comprise at least two terminal methyl groups (CH<sub>3</sub>) at each end of 10 the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, 15 isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acid esters are equivalent to those in branched-chain alkanes.

The CH functional group is equivalent to that of formic acid. The alkyl carboxylic acid ester C = O and C - C(O) groups are equivalent to those given in the Carboxylic Acids section. 20 The formic acid ester C = O group is equivalent to that given in the Carboxylic Acids section except that  $\overline{E}_{Kvib}$  is that corresponding to a formic acid ester. The C - O group is equivalent to that given in the Carboxylic Acids section except that the parameters corresponding to oscillation of the bond in the transition state,  $\overline{E}_D$  (eV) and  $\overline{E}_{Kvib}$ , are those of a carboxylic acid ester. As in the case with the alkyl ethers, each O - C group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the O AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the O - C H<sub>2</sub>-type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $c_2$  of Eq. (15.51) for the O - C-bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO to O) = 0.85395$ .

 $E_T \left( atom - atom, msp^3.AO \right)$  (Eq. (15.52)) of (1) the C = O group of alky carboxylic acid esters, (2) the C = O group of formic acid esters, (3) the alkyl carboxylic acid ester C - C(O) group, and (4) the carboxylic acid ester C - O group are equivalent to those of the corresponding carboxylic acids. The values given in the Carboxylic Acids section are  $-2.69893 \ eV$ ,  $-3.58557 \ eV$ ,  $-1.85836 \ eV$ , and  $-1.85836 \ eV$ , respectively.  $E_T \left( atom - atom, msp^3.AO \right)$  of the C - O group matches that of the C - C(O) group. Also, as in the case of aldehydes,  $C_{1e} = 2C_1$  in Eq. (15.52) for the C - C(O) group.

 $E_T(atom-atom, msp^3.AO)$  of the O-C-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is  $-1.13379\,eV$  for the  $O-CH_3$  group of 10 formate and alkyl carboxylates,  $-1.44915\,eV$  for the O-R group of alkyl carboxylates, and  $-1.85836\,eV$  for the O-R group of alkyl formates, where R is an alkyl group. Each is based on the energy match between the O AO, initially at the Coulomb potential of a proton and an electron (Eqs. (1.236) and (10.162), respectively), the  $C2sp^3$  HO of the methyl or alkyl ester group, and the carbonyl carbon. The increasing energy contributions to the single bond correspond to the increasing hybridization of linear combinations of increasing bond order. The energy contributions corresponding to one half of a double bond and those of the methyl-methyl and methylene-methylene bonds are  $-1.13379\,eV$  (Eq. (14.247)), two times  $-0.72457\,eV$  (Eq. (14.151)), and two times  $-0.92918\,eV$  (Eq. (14.513)), respectively.

The symbols of the functional groups of alkyl carboxylic acid esters are given in Table 15.105. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid esters are given in Tables 15.106, 15.107, and 15.108, respectively. The total energy of each alkyl carboxylic acid ester given in Table 15.109 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.108 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(Group)$  (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of alkyl carboxylic acid esters determined using Eqs. (15.79-15.108) are given in Table 15.110.

Table 15.105. The symbols of functional groups of alkyl carboxylic acid esters.

Table 15.105. The symbols of functional give	
Functional Group	Group Symbol
CH (formic acid ester) group	C-H (i)
C-C(0)	C-C(O)
C=O (formic acid ester)	C = O (i)
C=O (alkyl carboxylic acid ester)	C = O (ii)
(O)C-O	C-O
O-CH <sub>3</sub>	O-C (i)
O-R (formic acid ester)	<i>O – C</i> (ii)
O-R (alkyl acid ester)	<i>O – C</i> (iii)
OH group	ОН
CH <sub>3</sub> group	$C-H$ $(CH_3)$
CH₂ group	$C-H\left(CH_{2}\right)$
CH (alkyl) group	C-H (ii)
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

	fable 15.105. The geometrical bond parameters of ankyl carooxylle acid esters and experimental values.	The second	מוסטעלוות פבות בז	Sicas and dypolin	CILIST VALUED 11.											
C-H() C-C(0) C=O()	···	()) 0=	C=0 (ii)	0-0	0-0	0-(11)	0-c (iii)	$ C-H(CH_{*}) C-H(CH_{*})$	$C-H(CH_3)$	C-H (ii)	C-C (a)	(a) ン-ン	(e) C-C	(p) U-U	(e) U-U	(c) U-U
Group		Oroup	Group	Огонр	Group	Group	Стоир	Oroup	Group	Oroup	Group	Group	Growp	Group	Group	Group
2.04740	-	1,290799	1.29907	1,73490	1.82683	1.78255	11208.1	1.64920	1.67122	1.67465	2.12499	2,12499	2.10725	2.12499	2,10725	2.10725
1.43087	-	1.13613	1.13977	1,31716	09155.1	1,33512	1.34431	1.04856	1.05553	1.05661	1.45744	1.45744	1.45164	1.45744	1,45164	1.45164
1.51437		1.20243	1.20628	1.39402	1,43047	1,41303	1.42276	1.10974	1.11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1.53635
1.520 (scetie acid)		1.206 (methyl formate)	1.214 (acetic acid)	1.214 (ave. methyl farmate)	(ast. mediyi Somado	1.395 (avg. methyl formate)	1.393 (avg. methyl fomnate)	1.08 (methyl formate) 1,107 (C - H propane) 1,117 (C - H butane)	1.107 (C – H propane) 1.117 (C – H butene)	1.122 (isobutane)	(Juopane) 1,531 1,531 (butano)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
1,46439	ı	0.61267	0.62331	1.12915	1,22901	1.18107	1,20776	1,27295	1.29569	1.29924	1.54616	1.54616	1,52750	1.54616	1.52750	1.52750
0.69887	П	0.88018	187737	0.75921	0.73986	0.74900	0.74388	0.63580	0.63159	0.63095	0.68600	0,68600	0.68888	0.68600	0.68888	0.68888

Bond	Atom	I.	E,	r,	E	Final Total	],	7.3	Econom	E(C210")	ė	6	9	d,	þ
		(eV) Bond I	(eV) Bond 2	(eV) Band 3	(eV) Bond 4	Energy C2sp* (eV)	(°)	(જે	(eV) Finsi	(eV)	O	·C	·©	ૼ	· (°)
RC,(0)0-C,H,  (0-C (i))	0	ж 626'0-	.0.36640	0	O		1,00000	0,83360	-16.321/13		90.63	189,37	42.70	1,34246	0.00914
RC_(O)O - C,H, (O - C (I))	ڻ	06995.0-	c	p	o	-152.18239	147160	0,84392	.15.392KS	-15.20178	93.01	84.00	45.76	1,37445	0.07716
HC,(O)O – C,H,C,H,R (O – C (ii))	o	-0.9291K	-0.92918	0	0		1,00000	0.81349	-16.69412		93.09	16.91	43.59	1,29113	0.04399
HC,(O)O – C,H,C,H,R (O – C (ii))	ن:	40.920 EK	-0.92918	0	O	-153,47405	14616.0	0 X1549	-16,68411	.16,49325	93.09	86.91	43.59	1,29(13	0.04399
R'C, (0)0~C, H,C,H,R  (0~C (iii))	0	я1626.0-	-0.72457	0	0		1.00000	0.172562	16.47051		91.72	88.2X	43.10	131931	0.02480
R'C, (0)0 - C, H,C, H,R (0 - C (iii))	is*	-0.72457	*1626'0-	0	С	-153.26945	1,7710,0	0.82562	-16.47951	-16.28864	21.72	88.28	43.10	131751	0.02480
$HC_{*}(O) - OC_{*}H_{3}$ (C = O (1)) (O - C (1))	0	#1626.0·	-t) 56690	0	0		I. Datach	0,833/0	-16.321.83		70,87	81.03	46.82	1.18716	0.13000
HC,(O) - OC, H, (C = 0 (i)) (O - C (i))	ť.	40,9201R	-1.79278	0	C	-154.33765	0.91778	0.7733A	.17,54772	-17.35685	93.94	86.06	43.24	1,21386	0.05329
HC_(O) - OR (C = O (i)) (O-C (ii))	c	-0.92918	-0.929 ( 8	0	ū		1,0000	0.81549	- 16,68412		97.48	82.52	45.73	1,11100	0.10636
HC_(O) - OR ( C = O (i)) ( O - C (ii))	ن	41.7927F	40.92918	U	c	-15433765	17716.0	0.77536	1754771-	-17.35685	93.94	86.06	2,53	138%	0.03329
R'H,C,C,(O)-OC,H, (C=O (ii)) (O-C (i))	c	н (2Z6-0-	-0.56690	· u	o		1.0000	0.83360	.16,32183		98.97	£0,18	46.82	1.18714	0.13000
R'H,C,C,(O)-OC,H, (C=O (ii)) (O,-C (i))	r,	*!4 <b>[</b> 6.0-	-1,34946	#10.52.0.	c	-134.82352	0.91771	0.73447	•18,03358	-17,84271	96.19	88.04	41.90	1,29138	0.02578
$R'H_2G_c(O)-OC_bH_2C_rH_1R$ $(C=O\ (ii))$ $(O-C\ (iii))$	0	-0.92918	-0.72457	c c	0		1.00000	0.82562	-16,47051		94.33	11.68	K23	1.19766	0,11949
R'H,C,C,(0)-0C,H,C,H,R (C=0 (ii) (O-C (ii))	رځ	-0.92918	-1.34946	N1626.0-	0	-154.82352	0,91771	0.75447	-18,03358	17,84271	91.96	18.04	41.90	1,29138	0,02578
HC_(OR) = O (C = O (i))	0	-1.79278	0	0	o		1,00000	0.81871	-16,61853		137.10	42.90	65.45	0.53635	0.59978
HC_(OR) = O (C = O (i))	ر.	-1.7927K	41629.0	a .	o	-15433766	0.91771	0.77536	-17.54772	-17,33685	135.24	44,76	63.02	0,51361	0.55053
R'C,H'C,(OR) = O (C = O (ii))	0	94616-1-	0		o		1.00000	0.54115	-16,17521		12.70	42.73	1599	0.52193	0,61784
$R'C_nH_1C_n(OR) = 0$ (C = 0  (ii))	ڻ	1.34946	-0.9291X	-0.9291R	0	-154.82352	0.91771	0.75447	-17.03358	-17,84272	133.47	46.53	61.46	0.62072	0.51905
н -с(O)OR (сн (i))	را	1,792,1	-0.9291R	G	0	-154333766	0.91771	0.77536	-17.54772	-17,35685	69.89	11011	36.09	130373	0.16662
R'H,C, -C, (0)0R	٠٠	-0.92918	1.34146	105670-	0	-154,82352	0,91771	0,75447	-13.03358	-17,84272	56.25	123.75	15.37	1.85002	0.41915
H,C, -C,(0)0R	ر ا	-0.92918	٥	٥	•	.152.54487	0.91771	0,86359	-15,75493	-15.36407	72.77	107.73	34.17	1.69388	0.26301
C-H (CH.)	-	A1.929.18	-0.92918	0 0	0 0	-153.47405	0.91771	0.8(549	-16.68411	-16.49325	65.99	114.01	30.58	1.76270	0,331\$3
C-H (CH.)	- -	61,74,0)-	D O O			Append .	1//16'0	0.16359	-15.75493	15.56407	77.49	102.51	41.48	1,23564	0.11701
	-	#147Z'a1.	9167676	2	•	-133,47406	0.917/1	0,11349	-16.61412	-16,49325	68.47	111.53	35.84	135416	0.29933

Table 15.107. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid esters. R.R., R" are H or alkyl groups. E, is E, [ann - atom, nxy. AO].

Bond	Atom	L.	4	2		Final Total									
		: 5	: 3	} {	<u> </u>	Enemy	<u>]</u>	1	C. C. C.	E(C2sp')		φ,	φ,	9	ď
		Bond 1	Bond 2	Bond 3	Bond 4	É	(a)	<u>e</u>	(ev) Final	Final Final	ε	C	©	(°)	ં
C-H (CH) GD						٩									
(2) (2.2)	-	#16761b	-0.0Z91R	-0.92918	o	-154.40324	0.91771	0,77247	-17,61330	-17.42244	61.10	118.90	31.37	1.42918	0.37326
$H_{s}^{s}(\cdot,H_{s},H_{s}^{s}-(C-C,a))$	υ,	-0.92918	5	•	٥	-152.54487	12416'0	0,16359	-15.75493	-15.56407	51.0	116.18	30.08	1,83179	0.31106
H,C,C,H,C'H,=- (C'-C,(a))	ن	#1626.0+	K1626.0-	. 0	۰	-153.47406	0.91771	0.81549	-16.68412	-16,49325	56.41	123.59	26.06	068067	045117
(C-C'(b))	ن	-0.9291E	4,92918	*10Z0.0-	0	-154,40324	0.9177	0,77247	-17,61330	-17.42244	48.30	131,70	21.90	1.97162	0.51388
$(V - H_2C_2(W - H_2C_2)C_3(W - H_2C_2)CH_2 - (V - C_2)C_2(G_2)$	ڻ	#1626'B+	-0.72457	-0.72457	-0.73457	.154.71860	171160	0.75880	-17,92866	677.TJ.	48.21	131.79	21.74	1,587	0.50570
150C C. (H.C 11.) HCH															
((p).)))	ن	.0.9201я	-0.92918	410 <u>5</u> 0,0.	c	154,40324	0.91771	0,77247	-17,61330	-17,42344	48.30	131.70	21.90	1.97162	0.5138%
$(C - C \cdot (e))$ $(C - C \cdot (e))$	ن	-0.72457	-0,72457	-0.72457	-0,72457	.134,51399	17719.0	0.76765	-17.92866	977.71.	\$0.D4	129.96	22.66	1.94462	0.49298
ler(C, C, (H, C, -R) H C H, - $(C, -C, (0))$	۲,	-0,72457	21929.ft	A.92918	ď	-134,19863	17716.0	0.78155	-17.40KG	-17.21715	52.78	17.72	76.04	1.92443	0.47279
$kac.(R-H_1C_s)C_s(R-H_2C_s)CH_2-$	ť	-0.72457	-0,72457	-0.72457	-0.72457	-154.31399	0.91771	0.76763	-17.92KGG	017.73.719	\$0.04	120.96	22.66	1.94462	0.49291
										-			_		

Parameters	37																
	Group			(ii)	و د و د د	(C) = 10 - 10 - 10 - 10 - 10 - 10 - 10 - 10	(II) 0-0	(ii)	CH,	CH,	(I) H-2	(a) 2-2	(Q) )-)	(9) 2-2	(P) 2-2	(e) C-C	(i) 2-2
2	-	╀	. .					diagram	Group	Group	dror5	Croup	Group	Group	Group	Oroup	Group
	-	-	7	2	-	-		-	"	7	_	-	_	-	I	-	<u> </u>
n,	0	•	0	0	0	۰	٥	0	7	-	٥	6	•				
η,	0	۰	0	٥	٥	٥	٥		c	6			,	>	,	5	٥
ָיָ	0.75	0.5	0.5	0.5	0.5	0.5	\$6	*	, ,	22.0	250	3	3	5	0	0	٥
ن ً	-	-	-	-	-	-		3		0.73	0.73	S	50	50	0.5	0,5	0,5
	-	. -	-		- -	-		-	-	-	-		1	1	_	1	
,,		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	<u></u>
1	1//16/0	0.91771	0.85395	0.85395	0.85395	0.85395	0.85395	0.85395	0.91771	(7716.0	17716,0	0.91771	17716.0	17716.0	0.91771	0.91771	17710
	•	•	2	2	٥	٥	0	0	0	-	-	0	0		-	-	
	-	2	4	4	2	2	2	2	-	-	-	2	7	7	7		,
5	-	٥	٥	٥	٥	٥	0	C	m	2	-	0	0				
2,	0 73	-	0.5	0.5	0.5	0,5	0.5	0.5	0.75	0.73	0.73	3	3	2	٤	,   ;	,
	-	-	-	-	-	-	-	-	-	-	-	-	-	-	! -	3 -	3
(46)	-36.74167	-30.19634	-112.61934	-111,25473	-35.08488	-32.67173	-33.78830	-33.15757	-107.32728	-70.41425	-35,12015	-28.79214	-28 79214	-29 10112	23 70014	10 101	
r, (cV)	13.11890	9,50874	23.95107	23.87467	10,32968	10.06642	02061.01	10,12103	38.92728	25.78002	12.87680	9 33357	0 11117	0 27773	555.0		22.10112
1 (cV)	11.38634	7,57432	43.62589	42,82081	10.11150	8.94219	9.47754	9.17389	32,53914	21.06675	10.48582	6 77464	6 77464	60000	755557	67756	5/2/6.6
(aV)	-5.69317	-3.68716	-21.81195	-21.41040	-5.05575	4.47110	-4.73877	-4.58695	-16.26957	-10 53317	10076 5-	-1 10737	2 20737	2000	0.77404	0.5050	0.505.0
E( " m) (cV)	-14.63489	-14.63489	0	0	-14.63489	-14.63489	-14.63489	-14.63489	15.56407	-15 \$6407	-14 63480	15 55407	10 62407	DETCO'S.	76/80-0-	-5,45750	-3.45250
Atuin (w) in (eV)	-0.92918	0	-3.38557	-2.69893	-2.69893	-1.13379	-1.85836	-1.44915	6	-	2010	10,0000	13.30407	-13.33940	-13.56407	-15.35946	-1535946
Er (-1 10) (cV)	-13,70571	-14,63489	3.58557	2.69893	-11.93596	01102 61-	12 77653	12 19574	100000	,	,		•	5	٥	٥	٥
I'r (num) (aV)	-31,63530	-31.63534	-63.27075	-63.27074	-31.63541	11.873.15.	31,6367	21 62623	13,30407	13,30407	-[4.65489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
E. (atom - atom, usp. AO) (cV)	•	-1.85836	-3 58557	-2 60803	72838 T	QL C C I	20000	Creco.ic.	10,0070-	-49,00493	-51.03533	-31.63537	-31.63537	-31.63535	-31,63537	-31.63535	-31.63535
12, (sm) (aV)	31,63537	-33.49373	OF NEG TO	77070 59	בה לפוים, רב	21.037	-1.85850	-1.44915	0	•	0	-1.85836	-1,85836	-1.44915	-1.85836	-1.44915	-1.44915
(2) (10" rad (3)	36.0678	13 230	2000	200000	23,443,73	0160/75	.35.49373	-55.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33,49373	-33.08452	-33,49373	-33.08452	-33.08452
E. (aV)	03131 21	16.36.63	1905.00	39,4034	12,7926	21.4553	22,7749	12,0329	24.9286	24.2751	24.1759	9.43699	9,43699	15.4846	9.43699	9.55643	9.55643
F. (aV)	0,0000	אספר ת	071700	39,100,34	0.024.8	14,12224	14.99085	7.92028	16.40846	15,97831	15.91299	6,21159	621129	10.19220	621129	629021	6.29021
F. (eV)	0.35532		2015	-0.40004	977610	-0.24302	-0.23655	-0.18420	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
	(Eq. (13.458))	0.10502 [29]	0.21747 (52)	0.21077	0.14%5	(32)	0.11469	0.16118	(Eq.	(Eq.	0,35532 (Eq	0.12512	0.17978	0.09944	0.12512	0.12312	0.12312
$E_{nc}$ (eV)	-0.08153	-0.20715	-0.31017	-0.30266	-0.11745	-0.18628	-0.19921	-0.10361	-0.22757	-0.14502	-0.07200	0 10359	965600	7 1 5027	0 103 60	2	2000
(ab)	0.14803	0.14803	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0 14803	0 14803	14803	100710	2007	7,000	-0.1033y	-0.10260	-0.10260
E, (inm) (cV)	-31,71690	-33,70088	-67.47664	-66.57498	-33,61118	-32.95544	¥0209 : :-	218812	47 00 00 7	200000	2. 1000	0.14903	0.14803	0.14803	0.14803	0.14803	0.14803
Ennals, wim (eV)	-14.63489	-14.63489	-14.63489	-14,63489	-14,63489	-14,63489	-14 67489	╁	+	╁	10/0/15	25.59/32	╌┼	-33.24376	-33.59752	-35.18712	-33.18712
Franch le . vo an) (aV)	-13.59844	0	٥	٥	0	•	-	╀	╫	+-	100000	14.03489	-14.03489	-14.63489	-14.63489	-14.63489	-14,63489
Entra+ (cV)	3,48357	4.43110	8.70826	7.80660	4 34141	3 68 5 6	4 47314		╁	+	13.39844	٥	•	•	-	•	0
							0167	2.91632	14,49180	01068.	3.32601	432754	4.29921	3.97398	4.17951	3.62128	3.91734

Table 15.108. The energy parameters (eV) of functional groups of alkyl carboxylic acid exters.

١.	Attention of the second of the	mays caroun	THE BOIL CALL	2	al values [1].	in the calculation	or e., the para	ancters from th	e precoding	angle were	used, 6, i	1 Er (atom -	atom, nisp. AO).					
	Zc.	Zc.	E	Atom 1 Hybridization	100	Atom 2 Hehrldinalon	.r.	3	כי	ບົ	ن	v	Z.	6	9	$\vdash$	Cal. 0	Exp. 0
_	(g)	ν(α°)		Designation	Vises 2	Designation	Alora (	Alem 2	,	•		•	(6)	· ©	· ©		Ē	c
-				(Table 15.3.A)		(Table 15.3.A)								:	;	_		
1,00,11	1.70521	3,9463	-15.75493	7	-13.61806	0	O.KG.SU	0.83395 (Eq. (15.114))	87,0	-	0.75	0.91814	٥				109.95 (m	110 (methyl formate)
מעננ	15450.5	4,4043	-16.61K33 O.	α	الدوهواري ص	n	0,81871	0.11549	-	-	_	0.81710	9/559/1-			1	35.71	127
2.70321	1.63431	4,4833	-16.32183 C.	2	-18.47690 C,	es .	0,83360	0,73637	_	-	-	0.78498	-1.K5836				114.27	11d
211106	2.11106	3,433	-(5,754)3	7	=	я	0.86359	-	-	-	0.75	1.15796	0		$\top$	1	108.44	(propane)
														160			110.49	112 (propage) 113.g (bulane) 110.g
														15.69		<del>                                     </del>	110.49	(bulane)
2.09711	2.09711	3.4252	-15.75493	7	=	=	0.86359	-	-	-	0.75	1.15796	0		$\dagger$		05.001	(sobstanc)
														70.56	T	T	1004	(accumo)
-														70.36	T	$\dagger$	100.44	
2.91347	2.91547	4,7958	-16,68412 C,	a	-16.64412 C	ฆ	0.81549	0.81549	-	-	-	0.81549	-1.85836				┾-	110.8
2.91547	2,11323	4,1633	-15,55033 C,	•	-14.82575 C,	-	0.87495	17716.0	0.75	-	0.75	1.04887	0		T	Ť	92'911	
291547	2,09711	4.1633	-15,55033 C.	3	-14.82375 C <sub>c</sub>	_	0.87495	12216.0	0.75	-	67.0	1.04187	0			-	111.27	(isoburne)
2.90327	2.90327	4.795R	.15.55033 C.	ş	-۱۹.۳۵۶۶	-	0.87495	17716.0	0.75	-	0.75	1.04887	-1.15136			-	11.127	111.4
												1						/

AMIDES  $(C_n H_{2n+1} NO, n = 1, 2, 3, 4, 5...\infty)$ 

The alkyl amides,  $C_n H_{2n+1} NO$ , comprise a C = O functional group, and the single bond of carbon to the carbonyl carbon atom, C-C(O), is also a functional group. Formamide has a HC = O moiety that comprises a more stable C = O functional group and a CH functional 5 group that is equivalent to that of the CH (i) of aldehydes given in the corresponding section. It is also equivalent to that of the iso-CH group of branched-chain-alkyl portion of the alkyl amide except that  $E_{mog}$  (Eq. (15.58)) is not subtracted from  $E_D(Group)$ . All amides further comprise a  $C-NH_2$  moiety that comprises a  $NH_2$  functional group and two types of C-Nfunctional groups, one for formamide and the other for alkyl amides ( $RC(O)NH_2$  where R is 10 alkyl). The alkyl portion of the alkyl amide may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH)functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain 15 alkanes. In addition, the C-C bonds within isopropyl ( $(CH_3)_2CH$ ) and t-butyl ( $(CH_3)_3C$ ) groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in amides are equivalent to those in branched-chain alkanes.

The NH<sub>2</sub> functional group was solved in the Dihydrogen Nitride (NH<sub>2</sub>) section except 20 that the energy of the N-H MO is matched to the nitrogen-atom contribution to ΔE<sub>H,MO</sub> (AOIHO) and E<sub>T</sub> (atom-atom, msp<sup>3</sup>.AO) of the C-N group. Both alkyl amide C = O groups and the C-C(O) group are equivalent to those given in the Carboxylic Acid Esters section except that  $\bar{E}_{Kvih}$  of the C-C(O) group is matched to that of an amide. The C-N groups are equivalent to those of alkyl amines given in the corresponding section except that the energy of the C-N MO is matched to that of the C = O group and  $\bar{E}_{Kvih}$  is that of a amide.  $\Delta E_{H_1MO}$  (AOIHO) of the C-N group is equal to  $E_T$  (atom-atom, msp<sup>3</sup>.AO) of the alkyl C = O and C-N groups in order to match the energies of the corresponding MOs.

As in the case of primary amines, each C - N group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of

electrons between the  $C2sp^3$  HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the C-N  $H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $c_2$  of Eq. (15.52) for the C-N-bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO\ to\ N)=0.91140$ .

 $E_T(atom-atom, msp^3.AO)$  (Eq. (15.52)) of the C=O group of alky amides and the C=O group of formamide are equivalent to those of the corresponding carboxylic acids and esters. The values given in the Carboxylic Acids section are -2.69893~eV and -3.58557~eV, respectively.

 $E_T(atom-atom,msp^3.AO)$  of the amide C-C(O) group is the same as alkanes, 10 aldehydes, carboxylic acids, and carboxylic acid esters,  $-1.85836\,eV$ , where both energy contributions are given by Eq. (14.513). Also, as in the case of aldehydes,  $C_{1o}=2C_1$  in Eq. (15.52).

In order to match energy throughout the chain of the amide molecule,  $E_T(atom-atom,msp^3.AO)$  of the C-N-bond MO in Eq. (15.52) due to the charge donation 15 from the C and N atoms to the MO is  $-1.65376 \, eV$ . It is based on the energy match between the  $C2sp^3$  HO of the carbonyl and the primary amino group  $NH_2$ . It is given by the linear combination of  $-0.92918 \, eV$  (Eq. (14.513)) which matches the contiguous C-C(O) or HC(O) group and  $-0.72457 \, eV$  (Eq. (14.151)), the contribution of a primary amino group given in the Primary Amines section.

The symbols of the functional groups of alkyl amides are given in Table 15.111. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl amides are given in Tables 15.112, 15.113, and 15.114, respectively. The total energy of each alkyl amide given in Table 15.115 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.114 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl amides determined using Eqs. (15.79-15.108) are given in Table 15.116.

Table 15.111. The symbols of functional groups of alkyl amides.

Functional Group	Group Symbol
CH (formamide) group	C-H (i)
C-C(O)	C-C(O)
C=O (formamide)	C = O (i)
C=O (alkyl amide)	C = O (ii)
(O)C-N (formamide)	C-N (i)
(O)C-N (alkyl amide)	C-N (ii)
NH₂ group	$NH_2$
CH <sub>3</sub> group	$C-H\left(CH_{3}\right)$
CH <sub>2</sub> group	$C-H$ $(CH_2)$
CH (alkyl) group	C-H (ii)
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

_	_							
C-C (f)	2 10736	2701.7	1.43104		1.532 (propane)	(hutane)		132/30
C-C (e) Group	2 10736	1,46164	1.53635		L.532 (propane)	(butane)	0.000	06/36/1
C-C (d)	2 12400	1 45744	1.54280		1.532 (propane)	(butzme)	1 5/2/2	0100-
C-C (c) Group	2.10725	1 45164	1.53635		1.532 (propane)	(butane)	1 57750	22220
C-C (b)	2.12499	1.45744	1.54280		1.532 (propæse) 1.531	(buttue)	1 44616	0.68600
C ← C (a) Group	2.12499	1.45744	1.54280		1.532 (propane) 1.531	(butane)	1.54616	0 68600
C-H (ii)	1.67465	1.05661	1.11827		1.122 (fsobutane)		1.2924	0.63095
C-H (CH,)	1.67122	1.05553	1.11713		1.107 (C-H propane) 1.117	(C-H	1.29569	0.63159
C-H (CH <sub>3</sub> )	1.64920	1.04856	1,10974		1.107 (C – H propane) 1.117	(C~H	1.27295	0.63580
NH <sub>3</sub> Group	1,32297	0.97065	1.02729		1.027 (formamide) 1.022	(acetamide)	0.89894	0.73369
C-N (ii) Group	1.75370	1.32427	1,40155		(acetamide)		1.14968	0.75513
C-N() Group	1.70920	1,30736	1.38365		1.368 (formamide)		1.10098	0.76490
i) $C=O(il)$ $C-N(i)$ Group Group	1,29907	1.13977	1,20628		(acetamide) 1.225 (N-	methy tecctamode	0.62331	0.87737
dnoup ) O=2	1.290799	1.13613	1.20243		1.212 (formamide)		0.61267	0.88018
C-C(O) Group	2,04740	1,43087	1.51437	9131	(acetamide) 1.520	)	1.46439	0.69887
C-H(i) C	1,67465	1.03661	1,11827		1.125 (formanide)		1.29924	0.63095
Parameter	a (o,)	c. (o")	Bond Length 2c' (A)		Exp. Bond		h,c (a,)	

			,			-									
Hond	Аюн	/i, (eV) Bond I	<i>i</i> ; (eV) Bond 2	E, (eV) Bond 3	/;, (eV) Bond 4	Final Total Energy ("2sp" (eV)	) <u>e</u>	'∫ <u>(a,</u>	Econo (eV) Final	E(C2 $\psi^2$ ) (eV) Final	· (C)	' <sub>0</sub> (•)	(•)	(a, )	ć. (o)
RC(O)N(H) - H (C = O(i)  and (ii))	×	-0 83688	0	. 0	0		0.93084	0.86923	-15.65263		113.90	66.10	62.13	0.61843	0.322
$HC(O) - \lambda H_3$ ( $C = O$ (i) ( $C - N$ (j)	×	-0.K26##	¢	D	c		0.93084	0.16923	-15.63263		. 103.73	75,07	50.02	1.09214	0.20922
HC(O) = NH; (C = O (1)) (C = (O))	٠	-0 x76KK	-1.7927к	a	O	-154,23535	0.91771	0.77991	-17,44541	-17.25455	3,411	13.19	44.70	1.21492	0.09244
(C=0 (i)) (C-N (i))	2	-D.NZ6.NB	Đ	0	c		0,93084	0.16923	-15.63263		100.14	79.16	4R.10	1.17127	a.15300
RH_cC_C(O) – NH, (C = O (ii) (C - N (ii))	Ů,	-0.826ня	-1.34946	81 <i>626</i> 0-	0	154.72121	0.9177[	0.75878	-17.93127	-(7.7404)	90.51	89,49	4130	131755	0,00672
$HC_{i}(NH_{i})=0$ (C=O(i)) HC(NH)=0	0	-1,79278	0	0	0		1.00000	0.81871	-16.61833		137.10	42.90	65,43	0.53635	0.59971
(C=0 (i))	ن	.1.7927x	0.82588	a		-154,23533	0.91771	0.77991	-17,44541	-17.23455	135.44	44.56	63.28	0.58044	0.35569
(C=0 (ii))	a	1.34946	0	e	•		1.00000	0.84115	-16,17321		77.70	473	16.30	0.52193	0.61714
(C=0 (ii)	ij,	1,34946	-0 12611	#1026'0-	o	-134.72121	0.91771	0.75878	7218871.	-17,24041	133.67	16.33	61.70	0,61382	0.52395
(CH (0)		к7207.1-	-0.8368#	0		-154,23535	Q.91771	16624.0	11244,71-	17.25485	62.39	19,211	32.13	1,41810	0.36148
HC -C (0) NH	υ,	-0.92918	-1.34946	-0.8268я	٥	-154,72121	0.91771	0.75878	-17,93127	-17,74D41	\$7.02	18721	23.76	1,84586	0.41299
RH CH C = C (O)NH	٠.	-0.92918	٥	•	•	152.54487	0.91771	0.86359	-15.75493	13,56407	ונת	107.73	74.17	1.69388	0.25301
C-H (CH.)	٠	#1676'a-	x16760-	c .	• .	-153.47un5	0.91771	0.81549	-16.684f1	.16.49725	65.59	114,01	30.58	0.76270	0.33183
C - H (CH <sup>-</sup> )		aloca o	, 10,00	- 1	•	-152.54487	0.9[77]	0.86359	-15,75493	-15.56407	77.49	102.51	41.48	123564	0.15703
C-H (CH) (ii)		NICOLO OF	#1676'n-	20000	۰	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111,53	35.84	133486	0.29933
H.C.C.H.CH			BICTO.	41.9631B	-	136.4(1324	0.91771	0.77247	.(7,61330	17.42044	61.10	118.90	11.37	1,42911	0.37326
(C-C (a))	ن• ا	-0.92918		e		-132.54487	0.91771	0.86359	-15,75493	-15.36407	63.12	116.18	30,03	1,838.79	0.38106
((. – C (a))	ئ	81020.0-	-41,92918	۰	, ,	-133,47406	0.91771	0.81549	-16.68412	-16.49325	36,41	123.59	26.06	06806"	0,45117
$(C - C \cdot C_1)$ $(C - C \cdot C_2)$		*115Z6:0-	-0.9291x	-0.9291#	С	-154,40324	17716.0	0.77247	.17,61330	-17.42244	48.30	131.70	21.50	1,971@	0.51388
(C - C, C)	ئ	K1626'0"	-0.72457	-0.72457	-0.72457	-134.71860	17716.0	0.75889	.17.97866	ett.7.11-	7.7	131.79	21.74	NETZQ.I	0.50570
(C'-C'(d))	ئ	N1029.0-	-0.92918	-0,9291R	0	-154,40324	17716.0	0.77247	.17.61330	-17,42244	OC 17	131.70	21.30	1.97162	0.51388
(C-C'(e))	บ์	-0.72457	-0 72457	-0.72457	.0.72457	154,31399	14416.0	0.76763	33856.71.	errer.11.	50,04	129.96	22.66	1,944@	0.49293
ιστίζ, (Ηζί, - R')ΗCΗ <sub>2</sub> - (C - C' (f))	ئ	-0,72457	-0.92918	-0.9291я	ć	-154,19863	17710.0	0 78155	-17.40869	-17,21783	52.78	12723	80.2	1.92443	0.47279
$u \in \mathcal{L}(R^{-}H_{2}C_{2}) \cap \mathcal{L}(R^{-}H_{2}C_{2}) \cap \mathcal{L}(R^{-})$ (CC. (f))	۳	-0.72457	-0,72457	-0.72457 -	-0.72457	-154,51399	17710.0	0.76763	-17.92866	97757.71-	50.04	96'621	22.66	1 SAMO	0.49298
														-	•

Table 15.113. The MO to HO intercept geometrical bond parameters of alkyl amides. R.R., R" are H or alkyl groups. E, is E, (omm-uton, nsp', AO).

Table 15.114. The energy parameters (eV) of functional groups of alkyl amides.	ters (eV) of fun	ctional groups o	of alkyl amides.													
Parameters	C'-H (i) Group	C-C(O)	C=0 (i) Group	C=0 (ii) Group	.C-N (i) Group	C-N (ii)	NH, Group	£,	CH,	.C-H (ii)	C - C (a)	(4) 2-2	(e) J-J	(p) 2-2	(e)	0) 2-5
n,	-	-	7	7	_	-	2	- Canada	Croup	-	-	dio.	doop.	daoi	Group	dnog
ř.	۰	0	۰	۰	٥	6	•						-	-	-	-
Ę	٥		0	۰	6		,	1	-   «	9	٥	0	0	٥	0	٥
::	0.75	0.5	58	30	ž		1		,	,	٥	0	0	٥	٥	0
ن	-	-	-			3	5,70	6.73	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
, ,		-	-		-	- -	0.93613	-	-	-	-	-	-	-	-	-
	125.00		-	-	-	-	0.75	-	-	1.	1.	_	-	1	-	-
	0.91771	1//1670	0.85395	0.85395	0.91140	0.91140	-	0.91771	17716.0	17716.0	0.91771	17716.0	17716.0	17716.0	177160	17710
	-	ء ا	2	7	0	•	•	٥	-	-	0	٥	0	-	_	0
7		7	4	•	2	2	-	-	-	-	2	2	2	7	2	2
	-	0	0	٥	٥	٥	7	3	2	-	۰	0	٥	٥	٥	
	6.75	-	0.5	0.5	2.0	2	2	0.75	0.75	0.75	2,0	0.5	0.5	2.0	29	0.5
4	-	-	_]	-	-	-		1	-	-	-	-	-	-	-	-
(46)	-35.12015	-30.19634	-112,61934	-111.25473	-38.24008	-36.88558	-78.77719	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	20 101 12	70 101 17
( An) ''	12.87680	9.50874	23.95107	23.87467	10.40705	10,27417	28.03446	38.92728	25.78002	12,87680	9.33352	9.33352	9.37773	0 27757	246620	2000
((6))	10.48582	7.37432	43.62389	42.82081	11.18655	10.51650	29.77286	32.53914	21.06675	10.48582	77464	27777	00300	200000	2,312,5	5,312.0
r, (er)	-5.24291	-3.68716	-21.81195	-21,41040	-5.59327	-5.2822	-14.88643	-16.26957	-10.53337	-5.24291	-3.38752	338732	.345750	-3 18737	3.46360	2.45350
E.r. m) (eV)	-14.63489	-14,63489	0	0	-14.63489	-14.63489	-14,53414	-15.56407	-15.56407	-14.63489	-15 \$6407	15 55407	16 25046	201000	חסיייי	VC2645.
Min, wo (w) (eV)	0	•	-3.58557	-2.69893	-5,23932	4.35268	-1.65376	0	•	6		10.000	0466751	-15.50407	-13,35946	-13,35946
12 (a) m) (cV)	-14,63489	-14.63489	3,58557	2.69893	-9.39557	-10.28221	-17 88038	18 86407	16 66407	, ,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	,	,	>	-	•	٥
EL. 10 10) (cV)	0	0	٥		c	+	14 53414	13.3040	-13.30407	-14.03489	-15.56407	-13.36407	-15.35946	-15.56407	-15.35946	-15.35946
E, (u, m) (eV)	-31.65533	-31,63534	-63.27075	. PLUZ 2 19"	11 63533	21 63627	40 70 500			٥	•	0	0	٥	0	0
Er (alam - alam, msp', AO) (cV)	٥	-1.85836	-3 58997	20803	1 6627K	15550,15	-46.73008	167.6431	49,66493	-31,6353	-31.63537	-31,63537	-31.63535	-31.63537	-31.63535	-31.63535
Er(10) (eV)	-31 63537	-73 40173	05758 99	548407	11.03370	0/10001-	0	0	0	۰	-1:85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
(10,1 rad/x)	34 1260		200000	203.30500	-33.46914	-33.78912	48.73660	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33,49573	-33.08452	-33.08452
F. (aV)	15 01700	0.30040	186,700	39.4034	13.0822	12.5874	59.4067	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E (eV)	0 34066	00002.7	40.12300	35,10034	8.01093	8.28526	39.10250	16.40846	15.97831	15.91299	621159	651129	10.19220	621159	6.29021	6.29021
E. (cP)	0.35537	-0.40193	-0.41891	-0.40804	-0.19325	-0.18937	-0.39136	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
. Vale	(Eq. (13,458))	0.14655	0.21747 [32]	0.21077	0.17358	0.17358 [33]	0.40929	0.35532 (Eq.	0.35532 (Eq.	0.35532 (Eq.	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312
E., (cV)	-0.07200	-0.12867	-0.31017	-0.30266	-0.10647	-0 10278	-0 18672	0 22757	13,438)	(13.438))		3	Ξ	2	2	7
F., (eV)	0.14803	0,14803	0.11441	0.11441	0.14803	0.14803	0.14195	20871	2004302	0.2/0.0	-0.1033	-0.07526	-0.15924	-0.10339	-0.10260	-0.10260
Eybuny (eV)	-31.70737	-33.62241	-67.47664	-66.57408	-33 70550	†	201100	C. (*000)	0.14903	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
E (e, 10.100] (cV)	-14.63489	-14.63489	-14 67480	14 63480	14 (2400	+	+	-07.92207	49.80996	-31.70737	-35.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
E. L. 10 no) (cV)	-13.59844		0		604.07	-14.03403	-14,33414	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489
fintame) (eV)	3.47404	435263	8 7087.K	7 90660		+	+	-13.39844	-13.59844	-13.59844	0	0	٥	0	0	0
			0.110040	1.00000	4.12381	4.12212	7.37901	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

(c-c (e) C-C (d) Table 15.115. The total band energies of alkyl amides calculated using the functional group composition and the energies of Table 15.114 compared to the experimental values [3].

Formula Name C = H(i) C = C(i) C = O(i) C =

	Ехр. 9 (•)			119.2 (formanide)			125.0 (formamide)	(15.1 (sectareide)		122.0 (sectamide)	107 (propose)	(propend) (13.8 (butend) 110.8 (sebutanc)	(butane) (butane) (111,4 (feobutane)	10£.5 (pectore)			(110,5 (1sobutane)		(111,4 (isobadase)	(isobutane)	
	(e) (e)		108.27	118.61	119.04	116.18	124.91	116.63	124.63	121.95	108.64	110.49	110,49	109.50	109.44	109.44	19'011	92'011	111.27	111.27	107.50
	(e)																				
	e ©																				
	(E)											69.51	15'69		70.56	70.56					2.50
	E, (eV)		0	0	0	o	-1.44915	-1,41915	-1.63376	-1,44915	O			0			-1.85836	. 0	0	98858'1-	
E, is E, (alom - alom, msp' AO)	\$		1.06R23	0,98033	1.02006	\$2000	0.x3596	0.88749	0.K3472	0.23596	1.15796			1.13796			0.81549	1.04117	1.04187	L.OJERT	
. (atom - ata	J.		0.73	0.75	0.73	87.5	-	-	-	-	0.75			0.75			_	0.75	0.73	0.73	
d. Eris E	ڻ ا		-	_	-	-	-	-	-	-	-			-			-	-		-	
gle were use	נ'		-	27.0	0.75	0.7.5	1		1		-			-			-	675	0.75	0,75	
preceding an	C. Alon 3		-	17716.0	0.93613 (Eq. (15 62))	0.85395 (Eq.(15.114))	D K307H	0.91140 (Eq. (13.116))	0.85395 (Eq. (15.114))	0.H307B	-			-			0,81549	0.91776	0,91771	0,91771	
neters from the	ري. آ		0.93613 Eq. (15.62))	0.93613 (Eq. (15.62))	0.91771	177160	Siltro	สระจะบ	0.81349	SIIPED	0,86339			O,RG359			0.8154V	0,87475	\$5P48'0	\$ውැዘ'0	
ion of $\theta$ , the para	Atom 2 Hybridization Designation	(Table 15.3 A)	H	-	×	0	11	z	0	41	=			×			22	-	-	-	
the calculat	Ernamas Atras 3		н	-الزيو <sub>2573</sub> ر	-14.53414 N	-13,61806	.16.37720 N	-1433414 - N	-13.61906	.14,37720 N	=			x			) -  एक्स्पाउ	- 4.82375 (7,	-14,82575 C.	-14.82575	
ntal values [1]. I	Atom 1 Hybridization Designation	(Toble 15.3.A)	N	72	_	-	11	,	54	t)	,		i	,			æ.	s.	۶	5	
and experime	E. Alem 1		-14,53414	N 11785'71-	.) (',	-14,82575 C.	16,17321 O	-15.75493 (' <sub>b</sub>	16,680.11	14.17521 O	-13,75493			-15.75-813			1) (',	,) (°,	°,)	*,)	
lkyl amides	Zc." Terminal Amma (Q,)		3,1464	3,9328	4.0825	3.723%	43359.	N009'≯	4.3607	¥7157	3,4232			3,4252			4,7958	4.1633	4,1633	4,7958	
aneters of a	(a) E (c)		1.94130	1.94130	261473	ugu	261473	264835	2,37954	264155	711106			1,1707.1			2.91547	2.11323	2.09711	2,90327	
nd angle par	2c. (a,)		1.9130	2.61473	211323	2,11323	ונונדנ	2,86175	2.86175	1,27454	2.11106			111607			2,91547	2,91547	2.91547	2.90327	
Table 13.116. The bond angle parameters of alkyl amides and experimental values [1]. In the calculation of $ heta$ , the parameters from the preceding angle were used.	Almes of Argie	:	HNH7	$\mathcal{L}C_{\mu}(t); C_{\mu} = O(t)$	(CH (i): C, =0 (i))	CH (i))	(C, = 0 (I))	\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\\	((ii) (0 = ")) (i'.)*.)7	20C,N (C,=0 (ii))	H.JH7	15.5.57	H'.J'.77	H"JH7	7.1.17	н'.Г.т	'5".". '7'.'.'.'.'	H, C, H	H'.5')7	*5 pm *5",5",7"	'.Σ'.Σ'.Σ

## N-ALKYL AND N,N-DIALKYL-AMIDES ( $C_n H_{2n+1} NO, n=2,3,4,5...\infty$ )

The N-alkyl and N,N-dialkyl amides,  $C_n H_{2n+1} NO$ , comprise a C = O functional group, and the single bond of carbon to the carbonyl carbon atom, C - C(O), is also a functional group. Formamide has a HC = O moiety that comprises a more stable C = O functional group and a 5 CH functional group that is equivalent to that of the iso-CH group of branched-chain-alkyl portion of the N-alkyl or N,N-dialkyl amide. All amides further comprise a  $C - N(R_1)R_2$  moiety that comprises two types of C - N functional groups, one for formamide and the other for alkyl amides  $(RC(O)N(R_1)R_2)$  where R is alkyl). The N or N,N-dialkyl moiety comprises three additional groups depending on the alkyl substitution of the nitrogen. In the case of a 10 single methyl or alkyl substitution, the NH - C bond and NH are functional groups, and the N - C bond of a di-substituted nitrogen is the third.

The alkyl portion of the N-alkyl or N,N-dialkyl amide may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. 15 The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in N-alkyl or N,N-dialkyl amides are equivalent to those in branched-chain alkanes.

The NH functional group was solved in the Hydrogen Nitride (NH) section except that the energy of the N-H MO is matched to the nitrogen-atom contribution to  $\Delta E_{H,MO}(AO(HO))$  and  $E_T(atom-atom,msp^3.AO)$  of the C-N group. The C-C(O) group, both N-alkyl or N,N-dialkyl amide C=O groups, and both C-N groups are equivalent to those given in the 25 Amides section.

As in the case of primary amines, each N-C group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the N AO to form a MO permits each participating orbital to decrease in radius and energy. To meet the equipotential condition of the union of the

N-C  $H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $c_2$  of Eq. (15.52) for the N-C-bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO\ to\ N)=0.91140$ .

 $E_r(atom-atom, msp^3.AO)$  of the N-substituted amide C-C(O) group is the same as alkanes, aldehydes, carboxylic acids, carboxylic acid esters, and amides, -1.85836~eV, where both energy contributions are given by Eq. (14.513). Also, as in the case of aldehydes,  $C_{1o}=2C_1$  in Eq. (15.52).

 $E_T$  (atom – atom, msp<sup>3</sup>.AO) (Eq. (15.52)) of the C = O group of N-substituted alky amides and the C = O group of N-substituted formamide are equivalent to those of the corresponding carboxylic acids, carboxylic esters, and amides. The values given in the 10 Carboxylic Acids section are -2.69893 eV and -3.58557 eV, respectively.

 $E_T(atom-atom,msp^3.AO)$  of both C-N functional groups are the same as those of the corresponding groups of amides,  $-1.65376 \, eV$ .  $E_T(atom-atom,msp^3.AO)$  of the singly-substituted NH-C-bond MO in Eq. (15.52) due to the charge donation from the N and C atoms to the MO is  $-0.92918 \, eV$ . It is equivalent to that of tertiary amines and matches the energy of the NH-C group to that of the C-N group wherein  $E_T(atom-atom,msp^3.AO)$  of the latter is a linear combination of  $-0.92918 \, eV$  (Eq. (14.513)) and  $-0.72457 \, eV$  (Eq. (14.151)).  $E_T(atom-atom,msp^3.AO)$  of the doubly-substituted N-C-bond MO is  $-0.72457 \, eV$ . It is equivalent to that of the contribution of each atom of a primary amine and also matches the energy of the N-C group to that of the C-N group by matching one of the 20 components of  $E_T(atom-atom,msp^3.AO)$  of the latter.

The symbols of the functional groups of N-alkyl and N,N-dialkyl amides are given in Table 15.117. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of N-alkyl and N,N-dialkyl amides are given in Tables 15.118, 15.119, and 15.120, respectively. The total energy of each N-alkyl or N,N-dialkyl amide given in Table 15.121 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.120 corresponding to functional-group composition of the molecule. The bond angle parameters of N-alkyl and N,N-dialkyl amides determined using Eqs. (15.79-15.108) are given in Table 15.122.

Table 15.117. The symbols of functional groups of N-alkyl and N,N-dialkyl amides.

of in-airly and in, in-dialry and des.
Group Symbol
C-C(O)
C = O (i)
C = O (ii)
C-N (i)
C-N (ii)
NH
N-C (i)
N-C (ii)
$C-H\left(CH_{3}\right)$
$C-H(CH_2)$
C-H
C-C (a)
C-C (b)
C-C (c)
C-C (d)
C-C (e)
C-C (f)

Table 15.11	18. The geometr	Table 15.118. The geometrical bond parameters of N-alkyl and	ters of N-alkyl a	ind N,N-dialkyl :	unides and expe	N,N-dialkyl amides and experimental values [1]	[3]							,			
Parameter	Parameter C-C(U)	C=0()	(ii) (i=2)	C-N (i)	C-N (ii)	HN	N-C()	/ −C (ii)	N-C (ii) C-H (CH.) C-H (CH.)	C-H (CH.)	K-3	(0) ()-()	(a) .))	(6) .) – (6)	(q) C-C	(0) .) - (3	(C)
	Group		Group	Group	Group	Group	Group	Group			Group	Group	Group	Group	Great	Group	Group
		i							Group	Group							
a (a,)	2.04740	1.290799	1.29907	1.70920	1.75370	1.28620	1.96313	1.97794	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2.12499	2,10725	2,10725
0, (0,)	1.43087	1,13613	1.13977	1,30736	132427	0.95706	1,40112	1.40639	1.04836	1.05553	1.05661	1,45744	1.45744	1.45164	1.45744	1.45164	1.45164
Bond Length 2c' (A)	1.51437	1,20243	82902.1	1,38365	1.40155	1,01291	1,48288	1,48846	1,10974	61711.1	1.11827	1.54280	1.54280	1.53635	1.54280	1.5363	1.53635
Exp. Bond Length (A)	1,520 (N-mchyl- pcdesside)	1212 (formamide)	1,225 (N-makyl- socienik)	1.368 (farmamide)	LJBO (acciamidz)		1,469 (Nenefin)- sectomide)		1,107 (C-H propane) 1,117 (C-H butane)	1.107 (G-H propane) 1.117 (G-H butane)	1,122 (isobutane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1.532 (propane) 1.531 (butane)
b.c (n.)	1.46439	0,61267	0.62331	1,10098	1.14968	0.85927	1,37505	1,39079	1.27295	1,29560	1.29924	1.54616	1,54616	1.52750	1.54616	1.52750	1.52750
	0.69887	0.33013	757737	0.76490	0,75513	0.74410	0,71372	0.71104	0.63580	0,63159	0.63095	0,68600	0.68600	0.68888	0.68600	888890	0.68888

Alom E. E. E. E. E. E. E. E. E. E. E. E. E.	Alom	/5, (cV) Bond !	(cV) Bond 2	f, (cV) Bond 3	(eV) Bond 4	Finel Total Energy ('2y') (eV)		(a)	(eV) Finel	E((:24) <sup>2</sup> ) (eV) Final	. ©	(•)	(°)	(a, )	ر., (م.)
T.C.(1)N(C,R)-H C = O (i) and (ii) C - N (i) and (ii)	2	PACCOS S	464.59	e	s		0,93084	ns.2118	-16.11723		11547	(4.53	७८७	0,59403	0,36303
$\mathcal{C}_{\omega}(\Omega)\mathcal{N}(H) - \mathcal{C}_{\omega}H_{s}$ $\mathcal{C}_{\omega} = \Omega \ (0) \text{ and } (0)$ $\mathcal{C}_{\omega} - \mathcal{N} \ (0) \text{ and } (0)$	2	-th KCSvide	41 164 59	c	e ·		rutuš 0	Q NAZA ( )K	2711.91-		78.61	(E. 101	37,00	1.56779	0 16667
$C_{\omega}(O)N(H) - C_{\omega}H$ , $C_{\omega}(O)N(H) - C_{\omega}H$ , $C_{\omega}(O)N(H) - C_{\omega}H$ , $N_{\omega}(O)N(H) - C_{\omega}H$ ,	ئ	05 P7F 0"	e	c	c	12040251-	0.91771	Cyses U	רוטפר לו-	-15.09948	K3.37	69%	D) (70	1,50383	0.10271
*C_O() w(H) ~C,H,C,H,R C=O() and (ii) C~N() and (ii) N~C(ii)	2	יואלאניג	65747 0-	e	e ·		нажу	0,84318	-16.1172		32.61	UE, 101	37 (0	677.82.1	0.16667
C = O (1) and (ii)) C = O (1) and (ii)) C - N (1) and (ii)) N - C (1)	ڻ	(SP)† (r	H KGZ6 8"	e	e	4153 CR946	1421460	0.83,885	-16 21952	-14.02866	78.02	101.39	3664	1,57525	0 17413
PrC_(O)V(C,H,) - C,H, C = O (i) and (ii) C - N (i) and (ii) N - C (ii)	\$	X65Ex (F	הנבטיני סי	ፈርህያተ	c		<b>?388</b> 6'0	0.H3(7)	0£77£ 81-		75.57	104.43	38.35	161356	0.20697
TC_(O)N(C,H.) - C,H. C = O () and (ii) C = N () and (ii) N - C (ii)	ť.	4.1022)	s	c		-151.977XR	17714.0	0,89572	-15.18(0)	-14,99717	. KZ-59	97 41	39.70	1.52188	0.11549
$RC_{c}(t)N'(C,H,C,H,R)-C,H,$ C=O(t) and $(ii)C-N(t)$ and $(ii)N-C(t)$	2	HANGEN IT	622% ()*	GEENE'U'	=		A93uh4	0.33078	05775.201-		75.57	10443	15.35	1,61336	0.205.97
$C = C_1(G)N(C_1, C_2, H_1R) - C_1H_2$ $C = C_1(G) \text{ and } (G)$ $C = C_1(G) \text{ and } (G)$ $C = C_1(G) \text{ and } (G)$	ť	1136239	e	8	5	-151.9773#	וענופט	5850A.0	-15,15204	-14.99717	82.59	97.41	39.70	1,52188	0 11349
**C_((I)**([t]) - C,H,C,H,H C = O (() and (ii)) C - N (() and (ii)) N - C (ii)	· ×	MEJENIF	(CENT)	0.16229	· s		Ptoss'o	O.KUTA	05775.81-		13.57	19443	36.36	1.61336	0 25497
でこ(の)(R)ーC <sub>6</sub> H <sub>5</sub> C,H <sub>1</sub> R C = O (i) and (ii) C = N (i) and (ii)	ť	(£791)r	KIGZGU	g	c	-152-90716	ונופט	USALIR	-16.1172	15.92636	17.11	101.11	16.28	1.5945.1	0 16812
$VG_{c}(t) - N(H)R$ $C = O(1)$ $C = V(1)$ $C = V(1)$ $C = V(1)$ $C = V(1)$	2	ሂዳ97ሥ	65 PUT 17	=	С		780K U	מאייווצ	. KI1723		102.07	77.93	41.57	1.15050	0 176.77
$HG_{\alpha}(\Omega) - N(H)R$ $C = \Omega(0)$ $C = \Omega(0)$ N = C(0)	Ů	8297 K-C+	ж5267.1.	c	o	15423513	177.19.0	10977.0	18471	-17,23455	% ≅	(i (3)	£'.14	1,21491	H2700
$HC_{n}(\Omega) - N(R)R$ $C = \Omega(R)$ $C = N(R)$ $N - C(R)$ $R = nedigt or object$	2	TO NZGACE	4136220	4036129	٥		0.93084	Q.83078	05,772,01-		101.03	78.97	57.73	1,14842	0 15895
HC,(Ω) − N(R')R C = Ω (Ω) C − N (Ω) N − C (Ū)	ن	-0 K2688	**************************************	q	o	-154,23533	111160	19977.D	17.4541	-17.25455	18.88	PD:19	44.70	121492	0 09244

R. R. = methyl or allyl			-	-											
R'H,C,C,(M-N(H)R	L														
$ \begin{aligned} &(G=O\ (i)) \\ &(G-N\ (i)) \\ &(N-G\ (i)) \\ &(N-G\ (i)) \end{aligned} $	2	A1X.888	-0.46459		c		nama.	e man	52711.21-		78.f6	Z.	28 94	1.204dr	5,11562
$(R_{+}, C_{+}, C_{+}, C_{+}) = (R_{+}, C_{+}, C_{+}) = (C_{-} = 0, C_{+}) = (C_{-} = 0, C_{+}) = (C_{+} = 0, C_{$	ش,	-O.K 3G494	37GPE-1-	41 92918	c	1514,k1:	ותושה	0 75878	-17,93127	17072'21"	msi	89.49	4130	131755	0.00572
$R^{*}H_{s}C_{s}(C_{s}(O) - N(R))R$ (C = O (fi) (C - N (ii)) (N - C (fi)) $R^{*}R^{*} = \operatorname{inv}(h_{s}) \operatorname{de}(h_{s})$	×	-0.R3548	6. <u>C.S</u> X.0-	-0.36229			thank u	0 R107R	0 <u>2777.</u> 31-		77.06	11.93	45 87	02227	a. 10207
$R^{+}H_{\nu}G_{\nu}G_{\nu}(D) - M(R^{*})R$ $(C = D \cap (R))$ $(C = C \cap (R))$ $(N - C \cap (R))$ $R^{*}R = unethyt or alket$	ن	ים אכועצא	.1.34946	#1670 <b>&amp;</b>	q	154.73131	1431711	0.7587H	-17.20/127	117,74041	15,00	67'64	01.14	131355	0,00073
$HC_n(W(R^*)R^*) = 0$ (C = t) $(1)R^* = H nehyt, or oldytH^* = H nehyt, or oldyt$	0	MC507.1-	٥	С	a .		(Cara	158187	-16.61153		137.10	75.00	65.45	0.51635	Q.5997R
(C=0, V(R)) = 0 (C=0, R) $R, R = H, methyl, or allyl R \in H = 0$	ن	жт207.1-	MAN AND AND AND AND AND AND AND AND AND A	c	0	-15423535	0.91771	0.77991	1844,71.	-17.25465	13544	44.56	N. S.	0.38044	11.55569
$RC_{\mu}$ $A$	0	9761711-	c c		·e		L.Oxxxx	OMIIS	-16.17521		13.23	42.73	6631	0.52193	D61784
$(C_{\mu}, H, C_{\mu}, (N, K^{*}) = O)$ $(C_{\mu}, O, (i))$ $(C_{\mu}, O, (i))$ $(C_{\mu}, O, (i))$	ن	1.34946	ALREADY.	4162614	С	ומונדאפו.	0,91771	ATR\$C C	-17.93127	-17 74041	133.07	46.33	61.70	0.61582	0.52395
H - CON(R) R' R'.R" = H. methyl, or alkyl	نا	жг <u>с</u> 77.1-	********	e	o	-154,23533	4.91771	10077 0	17,44541	-17.25455	ų	113,61	12.13	0,41810	871960
R.R" = H. methyl, or alkyl	ن	41 929 IK	-1.34946	NACOST IT	0	-154.72121	111160	0 75K7R	Œ189 TI-	-17,74061	Sinis	12.98	25.76	1.1386	0.41299
17.4" = H. mellyl, or alkyl 11.1 C. H. C C. (1) M. (2)	ن	Al 92918		С	a	-152 54487	14160	0 863599	15,75493	18.36.07	1,17	tr.101	74.17	1.693KB	100,000
R.R. = H. methyl. or othyl	ن	н1929.1н	XICCUIT	в	. е	-153,47485	0,91771	0 RI 547	-16 68411	\$21Q\$ BI-	68.99	11401	30.58	1.76770	DIECE
C-H (CH)	٠	Alugan.	٠	t.	5	·152.5447	14160	0.45139	-15,75.03	15.5407	77.49	(S.E.)	41.48	1384	O. ISTOR
C-H (CH) (II)		20.271R	*1057.1*	e	٥	.153.474K	14160	0 81519	-16,64412	-16.49323	CH 47	11,53	35.84	1,15486	0.25933
H,C,C,H,CH, - H,C,C,H,CH, -	ن ر	WIGGG-	0	-0.7291K	c	-154,40124	17180	0.77247	0.819.71.	LE SOUTH	of. to	118.90	11.37	1,42388	911110
H.C.C.#.C.H - (CC. (a))	ť	и1с26.0-	405291X	c	e	Surre.té).	17716.0	0.81549	-16 (8412	-If. 49323	; \$	1 1 1 E	80 X	L.KURTO	901310
(CC. (b))	ن	410 <u>2</u> 018	48.0201x	-4 9291R	e	15(1875)	1771820	נענדם	-(7.61330	-17.42344	Q( 24	131.70	21.90	1.97162	0.51378
$(R-H_1C_1(R-H_1C_2)C_1(R-H_1C_2)CH_1-H_1C_2(R-H_1C_2)CH_2-H_1C_2(R-R_1C_2)$	Ü	A)626 G-	-0.72457	78157.0-	472437	-154,71860	17716.0	0.75279	-17.92%66	677.57.71	48.21	62,181	ZLM	1.95734	0.505.0
(ff. (d)) (ff. (d))	۳	*1026'0"	4,02918	419291K	5	rffur'h\$1·	17716.0	נידנו ס	-17.61330	17,4224	48.30	51.70	21.30	1.97162	Q.S.138R
(C - C (B))		75tf.th	751,17.0-	412457	12257	·154.51399	17710.0	O 767KS	-17.92166	67.77.11	50.74	129.96	3777	1.94462	0.49298
(C-C (D) (W-H C )C (R-H C )CH -	.:	יאונטי	419291X	4192914	ė	-134.17803	17716.0	D 7x155	-17.40%)	-17.21743	87.78	27.121	20 22	1.92413	041779
(C-C(0)	٠٠	472457	172,157	קפאבנה	73457	-154.51399	0.91771	0.7676	-17.92BC6	617.77.719	30.04	129.96	37.00	1.94462	0.49298
														1	

The state of the s								ľ									
Farances	Gamb Gamb	Group Group	C=(i) Group	() × - U	Group	WH Group	N-C()	ハーC (ii)	. E	- B	₹ g	(*) Organia Organia	(a) (a) (b) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c	() () () () () () ()	(1) (1) (2) (3) (3) (3) (4) (4) (4) (4) (4) (4) (4) (4) (4) (4	(e) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c	e gage
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	0.5	20	0.5	20	2,0	0.75	20	20	0.75	0.75	0.75	2	20	2	2	20	S
.,	-	_	-	-	-	0.93613	-	-	-	-		-	-	-	-	-	-
6.	-	-	1	-	-	0.75	1	_	-	-		-	-	-	-	-	-
ຮ້	17716.0	0.85395	0.85395	0.91140	0.91140	-	0.91140	0,91140	0.91771	17716.0	177160	17716.0	17710.0	17716.0	0.91771	17716.0	0.91771
ម៉	٥	1	7	0	0	-	0	0	o	_	-	0	۰	•	-	-	
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6	٥	٥	0	0	0	-	٥	٥	-	-	-	٥	0	0	•		
ť.	-	0.5	0.5	0.5	0.5	0.75	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0,5
, t	-	-	1	-	1	-	-	_	-	_		-	-	-	-	-	-
1, (el')	-30.19634	-112.61934	-111.25473	-38.24008	-36.88558	-40.92593	-31.67393	-31,36351	-107.32728	-70,41425	-35,12015	-28.79214	-28.79214	-29.10112	-28.79214	-29,10112	-29.10112
F, (eF)	9.50874	70156.62	1971875	10,40705	10,27417	1421618	19014'6	9.67426	38.92728	25.78002	12.87680	9,33352	9.3352	9,37273	933352	9.37273	637273
T (al')	7,37432	43.62380	42.52081	11.18655	10,51650	15.90963	8.06719	7.92833	32.53914	21.06675	10.48582	6.77464	6.77454	6.90500	6.77464	6.90500	6.90500
f. (e.F.)	-3.68716	-21.81195	-21.41040	-5.59327	-5.25825	7.95482	4.03359	-3,96416	-16.26957	-10.53337	-5,24291	-3,38732	3.38732	-3.45250	-1,38732	-3.45250	-3.45250
Elwind (el) .	-14.63489	0	0	-14.63489	-14.63489	-14.53414	-14.63489	-14,63489	-15.56407	-15,56407	-14.63489	-15.56407	-15.56407	-15.35946	-15,56407	-1535946	-15.35946
DEnisales m) (el)	0	-3.58557	-2 69893	-5 23932	4,35268	-1.65376	-0.92918	-0.72457	0	٥	٥	0	0	•	0	0	٥
E, Lo mi (cF)	-14.63489	3.58557	2,69893	-9.39557	-10,28221	-12.88038	-13.70571	-13,91032	-15.56407	-15.56407	-14 63489	-15.56407	-15.56407	-1535946	-15.56407	-15.35946	-1535946
F, lupol (e)')	-31.63534	-63,27075	-63,27074	.31.63533	31,63537	-31.63531	-31.63537	-31.63540	-67.69451	49.66493	-31.63533	-31.63537	-31.63537	-31,63535	-31.63537	-31,63535	31,63535
F. (atom - atom, m.g. Att) (eF.)	-1.85836	-3.58557	-2,69893	-1.65376	-1.65376	0	-0.92918	-0.72457	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1,44915	-1.44915
/;, [sm) (cl")	-33.49375	-66.85630	-65,96966	-33,28912	-33,28912	-31.63537	.32.56455	-32,35994	-67.69450	49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
(s/po. 101) a	14.1117	60.9581	59.4034	13.0822	12.5874	44,0494	10,6278	10,5037	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
(K, (eV)	9,28860	40.12366	39,10034	8.61093	8.28526	29.58649	6 99543	6,91703	16.40846	15.97831	15.91299	6,21159	6.21159	10.19220	621159	6.29021	6.29021
En (el)	-0.20195	-0.41891	-0.40804	-0.19325	-0.18957	-0.34043	-0.17039	-0.16837	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0,20896	-0.16515	-0.15416	-0.16416
$E_{\rm cut}$ (eF.)	0.14655 [28]	0.21747	0,21077 [21]	0.17358	0.17358	0.40696	0.12944 [23]	0 12944	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	(13.45g))	6.12312 [2]	0.17978 [4]	0.09944	0.12312 (2)	0.12312	0.12312 [2]
E, (cl)	-0.12867	-0.31017	-0.30266	-0.10647	-0.10278	-0.13695	-0.10567	-0.10365	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0,10359	-0.10260	-0.10260
E (c)')	0.14803	0,11441	0.11441	0.14803	0.14803	.0.14185	0.14803	0.14803	0,14803	0.14803	0.14503	0.14803	0,14803	0.14803	0.14803	0.14803	0.14203
$E_t \log_{-1} (e\Gamma)$	-33.62241	-67.47664	16725'99	-13,39559	-33,39190	-31.77332	-32.67032	-32,46359	-67.92207	-49,80996	-31,707,37	-33.59732	-33,49373	-33.24376	-33,59732	-33.18712	-33.18712
Franch, in 187 (e1')	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.53414	-14,63489	-14 63489	-14.63489	-14,63489	-14,63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489
Fandle wo mit (eV)	٥	0	0	0	٥	-13.59844	0	0	-13.59844	-13.59244	-13.59844	0	0	0	0	0	0
Epstempt (cF)	4,35263	8.70826	7.80660	4,12581	4,12212	3,49788	3.40044	3.19381	13.49186	7.83016	3,32601	4.32754	4.29921	3.97308	4.17951	3.62128	3.91734
Table 15, 121. The total band eners	res of N-dky	and N.N-dialky	d amides calcul	ated using the f	unctional groun	composition	nd the energie	s of Table 15.	120 compared a	o the experimen	trai volues (31						
Fremula Name C-C(D) CSO (1) CBC	(0)7-2	Cao (i)	7-3 0=	(i) C-N	HN	N-C()	۸-c (i)	C.¥,	7 C-N (1) C-N NH N-C (1) N-C (1) (H, CH, CH, C-C (1) C-C (1)	(E) (-)	(a) U-J	(3)	-J. (p) J	() C-C(0) C-C(0) C-C(0) C-C(0) C-C(0)	(f) Calculated	a Equinos	Relative
	Group	g S	es Greate	(E) O	dno.5										Charty	Ĕ,	Š

וו				Or (yullulum minut) and the property of the pr						0								
Lend 2	_	7.Cminst	1	Hybridgation	L'Company	Hybridization	ᢐ	ď	<del>ن</del>	ڻ	5	٠٧٠	£,	θ,	θ,		Cal. 6	Exp. θ
(")		_	T T	Designation T-h- 15 1 4)	View 3	Designation	Atma	Viole 5					( <sub>e</sub> )	Ξ	€ •	 ©	 ©	c
2.64835	1 2	63203	16.17521	12	-16.11722 N	11	0.84115	0.84418	-	-	-	0.84266	-1,44915		T	-	12.231	121.8 (N-methylacersmide)
3	264835	4.6904	-15.75493 C.	-	-14.53414 N	z	0.86339	0.91140 (Eq. (15.116))	-	-	-	0.88749	-1.44915				116.63	114.1 (N-methylacetamide)
L~	2,27954	4.5607	-16.68411	77	-13.61806	c	0.81549	0.85395 (Eq. (15.114))	-	-	-	0.83472	-1.65376		T	<del>                                     </del>	124.63	
	2.80224	4.6904	-17,93127 C,	\$	-16.219 <b>52</b> C,	4	0.75878	0.83885	-	-	-	0.79881	-1.83836				118.72 P	119.7 (N-methylacetamide)
	2.11106	3.4252	-15.75493	,	×	×	0.86339	-	-	-	0.75	1.15796	0		$\vdash$	<del> </del>	108.44	107
														69.31		-	67011	112 (propare) 113.8 (butane) 110.8 (trobutane)
								·						15.69			110.49	(butane) (11.4 (30butane)
	2.09711	3.4252	-15.75493	7	×	x	0,86159	-	-	-	0.75	1.15796	0		-	-	109.50	108.5 (acetone)
														70.56	-	-	109.44	
-														70.56		Ē	109.44	
	2,91547	4.7958	.16.68412 C.	\$1	-16.68412 C.	я	0.81549	0.81549	-	-	-	0.81549	-1.83836			<del>-</del>	110.67	110.8 (Eccbutane)
	2,11323	4.1633	-15.55033 C,	٠	-14.82575 C;	-	0.87495	17716.0	0.75	-	0.75	1.04887	٥		-	<del> -</del>	110.76	
	11260.2	4,1633	-15.55033 C <sub>b</sub>	s	-14.82575 C.		0,87495	12716.0	87.0	-	6.73	1.04687	0			-  -	111.27	11f.4 (isobutane)
	2.90327	4.7958	.13.55033 C.k	8	-14.82575 C,	-	0.87495	17716.0	87.0	-	6.73	1.04887	-1.85836			<u> </u>	111.27	111.4 (Isobutane)
			-											t S	ŀ	F	5	

UREA  $(CH_{\lambda}N_{\lambda}O)$ 

Urea,  $CH_4N_2O$ , comprises a C=O functional group and two  $C-NH_2$  moieties that each comprise a  $NH_2$  functional group and a C-N functional group. The C=O group is equivalent to that given for formamide in the Amides section except that the energy terms due to oscillation in the transition state are matched to that of urea. The  $NH_2$  and C-N functional groups are also equivalent to those given in the Amides section.  $E_T$  (atom-atom, msp<sup>3</sup>.AO) (Eq. (15.52)) of the C=O and C-N groups are equivalent to those of formamide. The values given in the Amides section are  $-3.58557 \, eV$ , and  $-1.65376 \, eV$ , respectively.

The symbols of the functional groups of urea are given in Table 15.123. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of urea are given in Tables 15.124, 15.125, and 15.126, respectively. The total energy of urea given in Table 15.127 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.126 corresponding to functional-group composition of the molecule. The bond angle parameters of urea determined using Eqs. (15.79-15.108) are given in Table 15.128.

Table 15.123. The symbols of functional groups of urea.

Group Symbol
C = O
C-N
$NH_2$

	. WH.	Group	1,32297	0.97063	1.02729	1,027 (formamide) 1,022 (acctamide)	0.89894	0,73309
and experimental values [1].	N-3	Group	1.70920	1,30736	1.38365	1.368 (formanide)	1.10098	0.76490
Table 19 174 The reometrical bond parameters of urea and experimental values [1]	0-3	Group	1.290799	1,13613	1,20243	1.212 (formamide)	0.61267	0.88018
Table 15 174 The reom	Parameter		u (u,)	c' (u,)	Bond Lenyth 2c' (A)	Exp. Bond Length	h, v. (u <sub>0</sub> )	3

Table 15 125. The MO to HO intercept geometrical band parameters of urea. $c_r$ is $c_r$ (s) $c_r$ (s) in the model of the mass $c_r$ is $c_r$	metrical br	and parameters o	1 WEE . C. 15 .	T (amm - amm	יומי אמוי				-			۱	,
The state of the s						Cinc Total	,		4	1, C. C. J. J.	ė	ъ,	Ď
Bond	Atom	نون	ri,	3	42	Lines 10m	1	1	2	1	3	. 3	ે ઉ
		5	<u>ئ</u>	(6V)	<u>§</u>	3 (	<u>e</u>	(°°)	Final	<u></u>	 E	_ E	=
		Bond (	Bond 2	Bond 3	Bond 4	43		:	<u> </u>	Final			
						7,69				_	9111	68.10	62.13
		0.07.00	•	0	0		0.93084	0.86323	15.65203				
H.NC(0)N(H)-H	٧	20000	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,				1000	reard o	1363331		103.93	76.07	<b>2002</b>
		437030	-	•	0	_	0.93084	0.00363	12,03600				-
H,NC(0)-NH,	2	20,000	,	-			1444	N TAAK!	PLCT # 81.	.18.08143	93.36	86.44	42.45
TIM VOYOU	:	-0 12633	-1.79278	-0.12688	0	133.00.413	47175	,					
カルハリーババン	-						1 00000	0.81871	-16.61853		137.00	g.	0343
H. NC (NH.) = 0	2	1.702.78	0	0	0	,			9000	10.001.62	1118	84.18	61.27
		97576	\$89C8 0	0.08888	0	-155.06223	0,91771	0.7640	-10.17.653	Calen's 1.			
H.MC (WH.)=0	<u>.</u>	-1.79178	000707	***************************************									

Table 15.126. The energy parameters (eV) of functional groups of urea-

Parameters	C = 0	C-N	NH <sub>2</sub>
	Group	Group	Group
n <sub>i</sub>	2	1	2
$n_{i}$	0	0	0
<i>n</i> <sub>3</sub>	0	0	1
C <sub>i</sub>	0.5	0.5	0.75
<i>C</i> ,	1	1	0.93613
<i>c</i> ,	1	1	0.75
<i>c</i> <sub>2</sub>	0.85395	0.91140	t
<i>c</i> <sub>3</sub>	2	0	0
<i>c</i> <sub>1</sub>	4	2	i
c,	0	0	2
C <sub>10</sub>	0.5	0.5	1.5
C <sub>2"</sub>	ı	1	1
V. (eV)	-112.61934	-38.24008	-78.77719
V <sub>p</sub> (eV)	23.95107	10.40705	28.03446
T (eV)	43.62389	11.18655	29.77286
$V_n$ (eV)	-21.81195	-5.59327	-14.88643
E(лотно) (eV)	0	-14.63489	-14.53414
$\Delta E_{H_2MO}(AOIHO)$ (eV)	-3.58557	-5.23932	-1.65376
$E_{\tau}(\lambda O(HO))$ (eV)	3.58557	-9.39557	-12.88038
E[1, 10140) (eV)	0	0	-14,53414
$E_{\gamma}(H,MO)$ (eV)	-63.27075	-31.63533	-48.73668
$E_{\tau}(alom-alom, msp^3.AO)$ (eV)	-3.58557	-1.65376	0
$E_{r}(m)$ (eV)	-66.85630	-33.28912	-48.73660
$\omega \left(10^{15} \ rad \ / \ s\right)$	19.9334	13.0822	59.4067
$E_{\kappa}$ (eV)	13.12053	8.61093	39.10250
$\bar{E}_{p}(eV)$	-0.23955	-0.19325	-0.39136
$ar{E}_{ extit{Kvib}}$ (eV)	0.21747 [32]	0.17358 [33]	0.40929 [22]
$\vec{E}_{\text{ex}}$ (eV)	-0.13081	-0.10647	-0.18672
$E_{max}(eV)$	0.11441	0.14803	0.14185
E, (Grap) (eV)	-67.11793	-33.39559	-49.11003
Einstal (c. AOTHO) (eV)	-14.63489	-14.63489	-14.53414
Einnat (c, AOIHI) (eV)	0	0	-13.59844
$E_{\nu}(Group)$ (eV)	8.34955	4.12581	7.37901

Table 15.127. The total bond energies of urea calculated using the functional group composition and the energies of Table 15.126 compared to the experimental values [3].

Formula	Name	C = O Group	C – N Group	NH <sub>2</sub> Group	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative Error
CH <sub>2</sub> N <sub>2</sub> O Urea		1	2	2	31,35919	31.393	0.00108

ie f. (atom - class men) (A)	- L ( min - min, ii.)	
as [1]. In the calculation of $ heta$ , the parameters from the preceding angle were used		Alom Alom 2
lable 15.128. The bond angle parameters of urea and experimental value	Abouts of Angle	7 37 37 37

			_	_	_		٠,	_
Exp. θ (°)					119.2	(/carried)/	(animating)	1250
(e) (c)	_		108 27			118.61		19761
e. O								_
ø_ ①								
0,⊙	_							
E <sub>T</sub> (eV)			5		-	•		1.44915
```		100	3		110260			0.835%
u-			2		0.75		ŀ	_
ď		-	-		_			_
ל		-			0,75			-
C <sub>1</sub> Aum 1		_			U9171		04000	W/0000
C <sub>2</sub>		0 93613	(2.1.2.)	-117100	(Fo (15,63))	House had	311720	
Atom 2 Hybridization Ocsignation	(I note (3.3.A)	×			_			
Friedmake Akm 2		Ξ		200	٦		02/27	2
Atom I Hybridization Designation	100000000000000000000000000000000000000	z			z		~	
Alson I		-14,53414		-14.53414	>	167(7)		•
Tennius Norm (U,)				10238			43359	
: <u>]</u>		65176		01.120			12727 2,6147	
(0)		1.54130		26(473	:		777777	
	COATE	מאט		EN.		77. 77	٠,٠	

## CARBOXYLIC ACID HALIDES $(C_n H_{2n-1}OX, X = F, Cl, Br, I; n = 1, 2, 3, 4, 5...\infty)$

The alkyl carboxylic acid halides,  $C_nH_{2n-1}OX$ , comprise a C=O functional group, and the single bond of carbon to the carbonyl carbon atom, C-C(O), is also a functional group. All carboxylic acid halides further comprise a C-X functional group where X is a halogen 5 atom. The alkyl portion of the alkyl carboxylic acid halide may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of 10 straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acids are equivalent to those in branched-chain alkanes.

The alkyl carboxylic acid halide C = O and C - C(O) groups are equivalent to those 15 given in the Aldehydes section and the Ketones section, respectively. The values of  $E_T(atom-atom, msp^3.AO)$  given in these sections are  $-2.69893 \, eV$  and  $-1.44915 \, eV$ , respectively.

As in the case of alkyl halides, each (O)C-X group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing 20 of electrons between the  $C2sp^3$  HO and the X AO to form a MO permits each participating orbital to decrease in radius and energy. For example, to meet the equipotential condition of the union of the (O)C-Cl  $H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $C_2$  of Eq. (15.52) for the (O)C-Cl-bond MO given by Eq. (15.111) is  $C_2(C2sp^3HO \ to \ Cl) = 0.81317$ . The solution is equivalent to that of the alkyl chloride bond except that the energy parameters corresponding to oscillation in the transition state are matched to those of a carboxylic acid chloride.

As in the case with the C-Cl group of alkyl chlorides,  $E_T(atom-atom, msp^3.AO)$  of the (O)C-Cl-bond MO in Eq. (15.52) of alky carboxylic acid chlorides due to the charge donation from the C and Cl atoms to the MO is  $-1.44915 \, eV$  where both energy contributions

are given by Eq. (14.511). This matches the energy of the C - C(O) functional group with that of the (O)C - Cl group within the carboxylic acid chloride molecule.

The symbols of the functional groups of alkyl carboxylic acid chlorides are given in Table 15.129. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid chlorides are given in Tables 15.130, 15.131, and 15.132, respectively. The total energy of each alkyl carboxylic acid chloride given in Table 15.133 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.132 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl carboxylic acid chlorides determined using Eqs. 10 (15.79-15.108) are given in Table 15.134.

C-C(O)
C=C(O)
C=C (alkyl carboxylic acid chloride)
(O)C-C1
CH, group
CH, group
CC band (n-C)
CC band (n-C)
CC (is no iso-C)
CC (it no i-C)
CC (it no i-C)
CC (it no i-C)

		The Part of Part of	_	chlorides and experimental values	ental values [11].							4) 0
Parameter	C C(O)	Table 15.130. The geometrical point parameters of any can both respectively. $C = C = C = C = C = C = C = C = C = C $	.,	C-H (CH,)	C-H (CH1)	Group	C-C(a) Group	Group Group	Group Group	Group	Oroup	Group
	Croup	35		Group	Croup	>74746	7 17499	2,12499	2.10725	2.12499	2,10725	2,10725
0 (0,)	2.04740	1.29907	2.32621	1.64920	1.0/122	1,0/402	1			145744	1 45164	1 45164
c. (a.)	1.43087	1,13977	1,69136	1.04856	1.05553	1.05661	1.45744	1.45744	1.45104	44/641	10101	
Bond	1,51437	1.20628	1,79005	1.10974	1,11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1,53635
3c. (A)							1 63.1	1 643	1 532	1.532	1.532	1.532
Exp. Bond Length	1.520 (acctone) (.518	(acetyl chloride)	1.798 (acetyl chlorid	(C-H propane) (C	(C-H propane)	1.122 (isobutane)	(propane) (.531	(propane)	(propane)	(propane) 1.531 (butane)	(propane) 1.531 (butane)	(propane) 1.531 (butane)
<u>?</u>	(2-butanone)	(neetic acid)		(C-H butane)	C - H butane)		Contanto	21712	1 57750	1 84616	1 52750	1,52750
h,c (u,)	1,46439	0.62331	1.59705	1,27295	1,29569	1.29924	1,34616	1.34010	064267	0.68600	0.68888	0,68888
	0 49887	0.87737	0.72709	0,63580	0,63159	0.63095	0.68600	0.58800	0.00000	7		

wo	20	07	/0:	510	078	3							6	50			
(a, )	0.30463	0.44625	0.61784	0.53901	0.39408	0.24675	0.1870\$	0,29933	0.37326	0.38106	0.45117	0.51388	0.505.0	0.51388	0.49298	0.47279	0.49298
(°,)	1.99599	2.13760	0.52193	0.60076	1.82495	1.67762	1.23564	1.35486	1,42988	1,83879	1.90890	1,97162	1,937.4	1.97162	1.94462	1,92443	1.94462
<b>6</b> ①	30.90	23.23	16,31	62.45	26.98	34.98	41.48	13.84	11,37	30.08	90'92	21.90	21.74	21.90	37.00	24.04	22.66
6 0	110.38	125.31	42.73	45.72	120.70	106.38	102.51	111.53	118.90	116.18	123.59	131.70	131.70	131.70	129.96	. 127.22	129.96
,6 °	69.62	54.69	137.27	134.28	59.30	73.62	77.49	68.47	61.10	63.82	17.93	48.30	48.21	48,30	\$0.04	52.78	80.0%
E(C2sp²) (eV) Final		-17,43350		-17,43350	-17.43350	.13.35946	-15.56407	.16.49325	- 17,42244	-15.56407	-16.49325	-17.47244	-17.73779	-17.42264	977 (7.7).	L8712.71-	ettt.t.1.
Ecuit (eV) Final	-15.55033	-17.62436	-16.17521	-17.62436	-17.52436	-15.55033	-15.75493	-16 68412	-17,61330	.15.73493	-16.68412	-17 61330	-17.92866	-17,61330 -	-17,92866	-17.40869	-17.92866
(e) [j.	0.87495	0.77199	0.84115	0,77199	0.77199	0.87495	0.86350	0.81549	0.77247	0.86359	0.81549	T+2TT.0	0.75#89	0.77247	0.76765	0.78155	0.76765
(°°)	1,05158	17716.0	1.00000	17710,0	17710.0	17710.0	17116.0	0.91771	0.91771	14416.0	14716.0	17716.0	0.91771	17710.0	0.91771	0.91771	0.91771
Final Total Energy C2sp <sup>3</sup> (eV)		-154.41430		-154.41430	-154.41430	-132.34026	152.54487	-153.47406	-154.40324	-152.54487	-153.47406	-154.40324	-154,71860	-154.40324	-154.51399	-154,19863	-154.51399
E <sub>7</sub> (eV) Bond 4	o	٥	0	0	0	0	0	0	٥	0	c	a	-0.72457	0	-0.72457	ó	-0.72457
E <sub>7</sub> (eV) Bond 3	•	-0.72457		-0.72457	-0.72457	0	. 0	0.	-0.92918	0	0.	91626.0.	-0.72457	-0.92918	-0.72457	-0.92918	-0.72457
(eV) Bond 2	•	-0.72457	0	-0.72457	-1.34946	0	0	-0.92918	-0.92918	0	-0.92918	40,92918	-0.72457	-0 92918	-0.TJAS7	\$1026.0-	-0.72437
(eV) Bond I	-0.72457	-1,34946	-1.34946	-1.34946	-0.72457	-0.72457	-0.92918	-0.92918	8162670-	-0.92918	8 (026 0-	-0.02918	-0 92918	.0 92918	-0.72457	-0.72457	-0.72457
Агот	ច	ئن	0	ť	ٔن	۲,		ر.	د	Ü	ڻ	٠,	ť.	نځ	ڻ	ڻ	ť
Волд	H,C,C, (0)-CI	H,C,C,(0)-CI	$H'C_sC_s(C_l) = 0$	$H_{r}C_{s}C_{s}(Ct)=0$	H,C, - C, (0) - C!	H,C, -C, (0) -C!	C-H (CH,)	C-H (CH <sub>1</sub> )	C-H (CH) (ii)	$H_1G_2G_3H_3CH_3 - (C-C^*(a))$	$H_iC_iC_iH_iCH_i$ –	$R - H_2C_2C_3(H_3C_2 - R^2)HCH_3 - (C_2C_2(b))$	$R - H_2C_*(R^- + I_2C_*)C_*(R^- + I_2C_*)C^-H_1$	$link, C_*(H_1C_* - R)HCH_1 - (C_* - C_*)$	$(C-C'(k))$ $(R-H_1C_2)C_4(R'-H_2C_2)C_4$	$(C'-C'(h_1C, -R')HCH_2 - (C'-C'(h))$	$isnC_{\sigma}(R^{*}-H_{1}C_{\sigma})C_{\sigma}(R^{*}-H_{2}C_{\sigma})CH_{2} (C^{*}-C^{*}(f))$

Table 15.131. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid chlorides.  $R_iR_i$ ,  $R^n$  are H or alkyl groups.  $E_f$  is  $E_f(alom-alom_i,mxp^2,AO)$ .

Table 15.132. The energy parameters (eV) of functional groups of alkyl ca	irs (ev) or tunctic	The property of the										
Parameters	C - C(O) Group	O=O Group	C-Cl Group	Group	CH <sub>2</sub> Group	ر <i>– H</i> (ii) Graup	C-C (a) Group	C - C (b) Group	C-C (c) Group	C-C (d)	C~C (e) Group	C-C (f) Group
i i	-	2	1	3	2	-	-	1	-	-	1	-
п,	0	0	0	7	-	0	0	0	0	o	0	0
j,	0	0	0	0	0	0	0	0	0	0	0	0
ر'	0.5	0.5	0.5	· 0.75	0.75	0.75	0.5	0.5	5.0	50	0.5	0.5
ئ	1	1	0.81317	1	1	-	1	1	1	1	1	
	-	-	1	ı	-	_	1	-	-	-	-	-
មា	0.91771	0.85395	1	17716.0	17710	0.91771	177160	0.91771	0.91771	0.91771	17716.0	0.91771
5	0	2	1	0	1	1	٥	0	0	-	-	0
5	3	4	2	1 .	1	1	2	2	2	7	2	2
5	0	0	0	3	2	1	0	0	0	0	0	0
<u>ت</u>	1	6.0	0.5	22.0	0.75	0.75	0.5	6.5	0.5	0.5	0.5	0.5
7.5	-	_	0.81317	-	-	1	-	1	_	-	-	-
V, (cV)	-30.19634	-111.25473	-29.68411	82226,701-	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	9,50874	25.87467	8.04432	38.92728	15.78002	12.87680	9,33352	9.33352	9.37275	9.33552	9.37273	9.37273
T (cV)	7.37432	42.82081	6.38036	- 32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_ (eV)	-3.68716	-21.41040	-3.19018	-16.26957	-10.53337	162423-	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(m m) (eV)	-14.63489	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15,35946
At u, se (so m) (aV)	0	-2.69893	-1.44915	0	0	0	0	0	0	0	0	0
Er (. m) (cV)	-14.63489	2.69893	-13.18574	-15.56407	-15.56407	-14,63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15.35946
$E_{\rm r}(u_{\rm i}\omega)$ (eV)	-31.63534	-63.27074	-31.63536	-67.69451	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31,63535
$E_r\left(\omega \omega m - \omega \omega n, m \varphi^2, AO\right) (eV)$	-1.44915	-2.69893	-1,44915	0	0	0	-1.83836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
$E_r(so)(cV)$	-33.08452	99696:59-	-33.08452	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33,49373	-33.08452	-33.08452
w (1013 rad 1.s) .	16.4962	59.4034	7,42995	24.9286	24.2751	24.1759	9,43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_{\kappa}$ (eV)	10.85807	39,10034	4.89052	16.40846	15.97831	15.91299	6,21159	6.21159	10.19220	6.21159	6.29021	6.29021
$\vec{E}_{n}$ (eV)	-0.21568	-0.40804	-0.14475	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.30896	-0,16515	-0.16416	-0.16416
E con (cV)	0.14655	0.21077	0.09063	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978 [4]	0.09944	0.12312	0.12312	0.12312 [2]
E. (eV)	-0.14240	-0.30266	-0.09943	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
f.mg (cV)	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803
Erbern (cV).	-33.22692	-66.57498	-33,18395	-67.92207	49.80996	-31,70737	-33.59732	-33.49373	-33.24376	-33,59732	-33.18712	-33.18712
Emand by . M III) (aV)	-14,63489	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489
Exemple, so mel (cV)	0	٥	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
En(rimmi) (eV)	3.95714	7.80660	3.76614	12.49186	7.83016	10925.5	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734

Table (5.133. The total bond energies of alky) carboxylic acid chlorides calculated using the functional group composition and the energies of Table (5.102 compared to the experimental values (3).

Formula Name C - C(0) C = C (c) C - C (e) C - C (e) C - C (e) C - C (f) C - C (c) C - C (e) C - C (f) C - C (f) C - C (e) C - C (f) C.H.CIO

Exp. θ	<u> </u>			111.6 (acetyl chloride)	121.2 (acety) chloride)	(auedoad) <i>L</i> O1	11.2 (propane) 113.8 (butane) 110.8 (isobutane)	111.0 (butane) 111.4 (isobutane)	108.6 (acatyl chloride) 108.5 (acetone)			110.8 " (sobutane)		1)1.4 (isobatane)	111.4 (isobutane)	
Cal. 9	<u> </u>		125.70	110,98	122.13	108.44	110,49	110.49	109.30	109.44	109.44	110.67	110.76	111.27	111.27	107.50
	<u></u>															
10	€															
60	<u> </u>						69.51	69.51		70.56	70.56					72.50
E,	્રું		-1.65376	-0.92918	-0.92918	0			o			-1.85836	0	0	-1.85836	
2,			0,83472	0.86359	0.84522	1.15796			1,15796			0.81549	1.04887	1.04887	1.04887	
ت				-	_	0.75			0.75			1	0.75	6.75	27.0	
ن			1	0.81317 (Eq. (15.111)	0.81317 (Eq. (15.111)	ı			1			1	-	-	-	
ບັ			1	ı	1	1			-			-	87.0	0.75	0.75	
σ.	Alom 2		0,85395 (Eq. (15.113))	0.86359	0,87495	1						0.81549	17716.0	12416.0	0.91771	
5	Alega		0.81540	0.86359	0.81549	0.86359			0,86359	i		0.81549	0.87495	0.87495	0.87495	
Atom 2 Hybridization	Designation	(Table 15.3.A)	0	כו	,	Н			н			25	-	-	1	
Contraste	Z may		-13,61806	-12,96764 (7)	13,55013	Ή.			π			-16.68412 C,	-14.82575 C <sub>h</sub>	-14.82575 C,	-14.82575 C,	
Atom I Hybridization	Designation	(Table 15.3.A)	7	,	52	7			,			я	<b>~</b>	w	\$	
F. roberto	Vicin I		-16.68411	-15.75493	-16.68412 ()	-15.75493			-15,75493			-16 68412 (',	-15,5503J (',	.،ء ععمىء در	-15.55033 C <sub>4</sub>	
2c' Terninal	_		4.5826	5.1539	4,9841	3.4252			3,4252			4.7958	4.1633	4.1633	4.7958	
2c.			2.27954	3,38271	1,38271	211106			2.09711			2.91547	2,11323	1.09711	1.90317	
2c° flend i	(%)		1.86175	2.86175	2.27954	2.11106			1.09711			2.91547	2.91547	2.91547	1,90327	
Assment Angle			כנינים	77.7.77	בנאכי"כנו	Methybre ZHC, H	ZC.C.C.	ZC,C,H	Madest ZHC,"H	;J*,J*,J	4C,C,H	حديدير. ته ري	70°C, H, 7,722	ZC,C,H In C,	حد:رد"ر. مرد"ر"	"C"C"C"

## CARBOXYLIC ACID ANHYDRIDES ( $C_n H_{2n-2} O_3$ , $n = 2,3,4,5...\infty$ )

The alkyl carboxylic acid anhydrides,  $C_nH_{2n-2}O_3$ , have two (O)C-O moieties that each comprise C=O and C-O functional groups. The single bond of carbon to the carbonyl carbon atom, C-C(O), is also a functional group. The alkyl portion of the alkyl carboxylic acid anhydride may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2CH)$  and t-butyl  $((CH_3)_3C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in carboxylic acid anhydrides are equivalent to those in branched-chain alkanes.

The alkyl carboxylic acid anhydride C = O and C - C(O) groups are equivalent to those given in the Carboxylic Acid Esters section and the Ketones section, respectively. The values of  $E_{\tau}(atom-atom,msp^3.AO)$  given in these sections are -2.69893~eV and -1.44915~eV, respectively. The C-O group is also equivalent to that given in the Carboxylic Acid Esters section except that  $E_{\tau}(atom-atom,msp^3.AO)$  is equivalent to that of an alkyl ether as given in the corresponding section and the energy terms due to oscillation in the transition state are matched to that of a carboxylic acid anhydride.

For the C-O group,  $E_T(atom-atom,msp^3.AO)$  is  $-1.65376\,eV$ . It is based on the energy match between the O AO and the  $C2sp^3$  HO of each C-C(O) group and is given by the linear combination of  $-0.72457\,eV$  (Eq. (14.151)) and  $-0.92918\,eV$  (Eq. (14.513)), respectively. This matches  $-0.72457\,eV$ , the energy contribution of each of the  $C2sp^3$  HOs to each C-C(O) functional group, with that of the corresponding energy component of the C-O group and gives a minimum energy within the carboxylic acid anhydride molecule.

The symbols of the functional groups of alkyl carboxylic acid anhydrides are given in Table 15.135. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl carboxylic acid anhydrides are given in Tables 15.136, 15.137, and 15.138, respectively. The total energy of each alkyl

carboxylic acid anhydride given in Table 15.139 was calculated as the sum over the integer multiple of each  $E_D(G_{roup})$  of Table 15.138 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl carboxylic acid anhydrides determined using Eqs. (15.79-15.108) are given in Table 15.140.

Table 15.135. The symbols of functional groups of alkyl carboxylic acid antydrides.	ups of alkyl carboxylic acid antydrides.	
Functional Oroup	Group Symbol	
C·C(O)	(2-0(0)	
C=O (alkyl carboxylic acid anhydride)	0.0	
0.0(0)	0-0	
CH, group	$C-H(CH_s)$	
CH; Group	C-H (CH;)	
CH (alkyl) group		
CC bond (n-C)	(0, .))	
CC bond (iso-C)	(9)	
CC bond (tert-C)	(3) .,,	
CC (iso to iso-C)	(a)	
CC (tip t-C)	((. (0)	
2000		

Furameter $C = C(0)$ Group Group Group		_	0-0 Oroup	C-0 (-H (rH,) (-H (CH,	(H (CH;)	ن − H Orono	(e) angly	(2) Supply	(e) U-U	ري-ر (ع)	(e) (j-(j-	() C-C
1,29907 1,73490 1,64920	1.73.490 1.64920	Group 1,64920	4	ق اق	Group 1,67122	-	2,12499	212499	2.10725	2.12499	2.10725	2.10725
1.43087 1.13977 1.31716 1.04856 1	1.31716 1.04856	1.04856		-	.05553	1,05661	1.45744	1.45744	1.45164	1,45744	1.45164	1.45164
1.51437 1.20628 1.39402 1.10974 1.	1.39402 1.10974	1,10974			1,11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1,53635
1.214 (C-H propane)	1.393 (C - H propane)	1.107 (C - H propane)		ن	1.107 H ortonane)	1.122	1.532 (monare)	1.532	1.532	1.532	1.532	1.532
	formate) (C - H butene)	(.117 (C-H butme)		ر ان	1.117 (C-H butone)	(isobutane)	1.531 (Butane)	1,531 (butanc)	(531 (butane)	(butane)	1.531 (furtane)	(Figure)
1.46439 0.62531 1.12915 1,27295	1.12915 1.27295	1,27295	_	-	.29569	1.29924	1,54616	1.54616	1,52750	1.54616	1.52750	1,52750
0.69887 0.87737 0.75921 0.65580	0.75921 0.63580	0.65580			0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0.68888	0.68888

Table 15.157. The MO to HO intercept geometrical bond parameters of alkyl carboxylic acid anhydrides. R.R., R. are H or alkyl groups. Et is Et are armining AO	netrical bon	nd parameters of	alkyl carboxylic	acid anhydrides.	K, K, K are	H or alkyl grot	ups. 2, 18 Lp.	atom - atom, n	rsp. VO).						
Bond	Атош	E,	E,	E,	7	Final Total	Jan.	Ĺ	Errating.	$E(C2sp^2)$	θ.		θ,	ď	ď
		(cV) Bond I	(eV) Band 2	(eV) Bond 3	(aV) Bond 4	C.C.s.p.*	(g)	(a,	Final	(eV) Final	©	©	©	(%)	(°°)
RC.H.C.(0)-0,-C.(0)C.H.R.	0	-0.KZKKK	-0.82688	٥	0		1,0000	0.82562	-16 47951		27.16	\$1.68	46,34	1.19766	0.11949
RC,H1C,(0)-0,-C,(0)C,H1R	٠٠	-D.K2GNII	-1.34946	-Q.RZKKR	0	-154.51600	17716.0	0.76753	-17.72667	-17,53580	93.21	16.79	47.74	127417	16ZNO'0
RC, H, (R'C, H,C, (O, )O)C, = O,	o'	1.34946	•				1,00000	0.84115	. 16.17521		137.27	42.73	66.31	0.52153	0,61784
$RC, H_1(R'C, H_1C_1(O_2)O)C_2 = O_2$	5	. 1 345df	4,72457	-0.K2GKR	0	15431660	17216.0	0.76753	-17.72667	.175380	134,08	45.92	62,20	0.60583	0.53394
RH,C, -C,(O)OC,(O)C,H,R'	٠٠	-0.72457	-1,34946	-0,42548	c	134,51600	17716.0	0.76753	17.72667	-17,53580	58.55	121.45	26,56	1,83133	0.40045
H,C, - C, (0)OC, (0)C,H,R'	ť	-0.72457	٥	o	0	-152,34026	17719.0	0.87495	-15.55033	15.35946	23.67	106.38	34.98	1,67762	0.34675
$RH_2C_s - C_s(O)OC_s(O)C_sH_sR^s$ $R = aR_sVl$	3	-0.72457	4192913	u	0	133,20945	122160	0.12562	-1647951	-16.2NR65	67,40	112.60	35.15	1.74821	46715.0
rH (CH,)	ر.	816Z6'0"	•	0	c	132.54487	- 12216'0	0,86359	15.75493	15.56407	69'11	12.001	41,48	13862.)	0,18703
( - H (CH,)	ر	-0.9291K	-0.9291X	в	0	153,47406	161931	0.81549	-16,68412	-16,49325	68.47	111.53	35.84	135476	0.29933
C-H (CH) (ii)	υ	.0,92913	-4.9291X	-0.9291#	D	154,4U324	1/21670	0.77247	-17,61330	-17,42244	61.10	118.70	1,51	1,42918	0,37326
H,C,C,H,C'H,	.5	-0.92918	u	c	G	.152.54487	0,91771	0.16339	.(5.73493	-13.56407	63.82	11618	30 08	ecres.	0.38106
$H_1C_1C_2H_2C_{H_2}$ – $(C-C_1(a))$	C,	-0,92918	жылы.	U	-0	33,47406	122150	6)\$13(0	-16.68412	-16,49325	36.41	123.59	26.06	1.90190	0,45117
$R - H_1(C,C,(H_2C,-R)HCH_3 - (C,-C,(b))$	5)	-0.92918	-0,9291R	#1020.0-	0	-154,40324	177160	0.77247	-17,61330	-17,42244	48.30	131.70	21.50	1,97162	0.51388
$(C - C')(R - H_2C_s)C_s(R^2 - H_2C_s)CH_3 - H_3C_s(R^2 - H_3C_s)CH_3 - H_$	ن .	-0,9291R	-0,72457	T2457.0-	-0.72457	-154.71860	17716.0	0.75119	-17.92866	61757,71-	48.21	131.79	21.74	LET28.1	0.50570
$(C-C', H_2C, -R')HCH_2 - (C-C', (d))$	ڻ	\$16Z6'U*	-0.9291X	81620.0-		-154,40324	0,9171	0,777247	-17,41330	-17,42344	4K.30	131.70	21.90	1.97162	0.51388
$(R' - H_2C_A)C_1(R' - H_3C_1)CH_1 - (C' - C' C_0)$	C.	-0,72457	-0.72457	-0.72457	-0.72457	-154,31399	0,91771	0,76765	-17.93266	-17.73779	\$0.0¢	36.62.1	22.66	1.94462	0.49298
$iere''.\zeta.(H.\zetaR)HCH_z-$ $(C'-\Gamma'(f))$	r,	-0,72457	#1020;0-	#1626'0-	· ·	-134.19863	17718.0	0,78155	-17.40169	-17.21783	\$2,71	27.71	24.04	1.9243	0.47279
$ int'_{1}(H-H_{2}C_{2})C_{1}(H'-H_{2}C_{2})CH_{2}- int'_{1}CH_{2}C_{2} $	3.	-0.72457	-0.72457	-0.72457	47,7457	-154.51599	17710.0	0.76765	-(7.92866	-17.73719	30,04	129.96	99 72	1.94462	0.49298

15.157. The MO to 10 intercent reconstricts bond carameters of alkel carboxelic acid anhydrides. R. R. are H or alkel crouns. E. is E. [atom=atom:man]. A

Table 15, 138. The energy parameters (eV) of functional proups of alkyl carboxylic acid nihydrides.	ers (eV) of function	anal proups of alky	oarboxylic acid	suhydrides.								
Parameters	(C)(C) Choub	0 ≡ 0 0 ± 0	0-0 Ugan	£.	 ₹	Group	Group	(a) (b) (c) (d) (d) (d) (d) (d) (d) (d) (d) (d) (d	Graup Graup	(g) diago	e age Ogge	Croup Group
	-		-	Cinon	die de		-	-	-	-	-	-
n,	-	3	-	٦	7	-	-	-	-		-	-
<i>u</i> ,	0	0	0	2	-	0	0	0	0	٥	c	0
n,	0	0	0	0	0	o	0	0	0	0	0	- 0
	0.5	5,0	0.5	0.75	0.75	0.75	5'0	0.5	6,5	0.5	0.5	0.5
ن	1	-	1	7	1	1	1	_	-	1	1	•
	1		1	-	1	1	1	-	-	-	1	-
	17716.0	0.85395	0.85395	17716.0	17716.0	17716.0	0.91771	0.91771	177160	17716.0	0.91771	17716.0
٠	0	2	a	o	1	1	0	o	0	-	-	0
ر.'	2	7	7	-	1	1	7	7	2	2	2	2
2.0	0	0	0	3.	7	1	0	0	0	0	0	
ال.	-	5'0	6.5	0.75	27.0	0.75	5'0	6.9	0.5	6.5	0.5	20
. A	1	1	-	1	1	1	1	1	1	1	1	
V, (eV)	-30.19634	-111,25473	-35.08488	107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10312	-29.10112
V, (aV)	9.50874	13,87467	10.32958	38,92728	25.78002	12,87680	533352	9.33352	9.37273	9,33352	9.37273	9.37275
T (aV)	7.37432	42.82031	10.11150	32.53914	21.06673	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V. (dr)	-3.68716	-21.41040	-5.03575	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3,45250
E(.m no) (eV)	-14.63489	0	-14.63489	-13,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	15.56407	-15.35946	-15.35946
DEngar (no no) (eV)	•	-2.69893	-2.69893	o	0	0	0	0	0	0	0	0
liplus no) (eV)	-14.63489	2,69893	-11.93596	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
L' (m, vo) (cV)	-31.63534	+63.27074	-31.63541	-67,69451	-49.66493	-31.63533	-31.63537	-31,63537	-31.63535	-31.63537	-31.63535	-31.63535
E, (atom - atom, msp2.AD) (eV)	-1,44915	-2.69893	-1.65376	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1,44915
έ <sub>τ</sub> (wo) (αV)	-33.08452	99696'59-	-33.28912	-67.69450	-49.66493	-31,63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
w (1015 mad ).s)	16.4962	59,4034	24.3637	24.9286	24.2751	24.1759	9.43699	9,43699	15.4846	9,43699	9.55643	9,55643
E (eV)	10.85807	39,10034	16.03660	16.40846	15.97831	15.91299	621129	6.21159	10.19220	6.21159	6.29021	6.29021
E, (eV)	-0.21568	-0.40804	-0.26373	-0.25352	-0.25017	-0.24966	\$1591.0-	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Exm (cV)	0.14655	7,012.0 [21]	0,13638	(Eq. (13.458))	0,35332 (Eq. (13.458))	0.35552 (Eq. ((3.458))	0.12312 [2]	0.17978	0.09944	0.12512 [2]	0.12312	0.12312 [2]
F., (cV)	-0.14240	-0.30266	· -0.19554	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
$E_{m,p}$ $(cV)$ .	0.14803	0.11441	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803
Eyformy (OV)	-33.22692	86578.99-	-33,48466	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
Emula, in not (cV)	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Emula, wo and (eV)	0	0	0	-13.59844	-13,59844	-13.59844	0	0	0	o	0	c
Entrany (cV)	3.95714	7.80660	4.21488	12.49186	7,83016	3.32601	\$\$17£\$	4.29921	3,97398	4.17951	3,62128	3.91734

version and angle parameters of alkyl carococylic acid anhydrides and experimental values [1]. In the coloulation of 0, the parameters from the preceding angle were used. E. is E. (anima men's sol	Other sugge	per america o	alkyi carox	ocylic acid as	shydrides and exp	erinental va	lucs [1]. In the cal	culation of $ heta$	, the parameter	rs from the p	receding an	gle were us	od E is E	fatom-atom "	(07,00)				
Park in the latest	žį	žÎ	2¢" Tensinal	Graduan	Atom 1 Hybridization	1,1	Atom 2 Hybridization	5	٠	0	Ú	ن	٧	E		٩		9	0 452
	(ં હ	(°°)	Amer (a,)	Į.	Designation (Table 15.3.A)	Ven 2	Designation (Table 15.1.4)	Į	Alera 2		•	-	,	<b>.</b> (§ †	. C	· ①	, 	<u></u>	į
0.507	1.27954	743431	43012	-16,17521	12	-16.47951	21	931178.0	63500	-					1	$\dagger$	1	1	
		╁		17,30634		-17 10612			70070'11	-]	- ]	-	0.k3339	-1,44915	_		_	00.221	(acctic technical)
۲۱ "۱٬۱٬ "	2.0.431	263431	1,4944	ئن	*	C	×	0.78517	0,71617	-	_	_	0.7146.17	.1.85836		-	+		115.8 (36)
70".37	2.86173	IEPEY?	1,4944	-15.55033	,	13,61206	c	0.07404	0.15395									60.	(seeds mindride)
0.5.57	2.86173	2376	1 676	1017	.   ;		,	C(#/4/)	(Eq (15.114))	-	-	-	0,86443	-1.44915			_	59.60	tox.3 [36]
Meth bue		┿		-10.4723	71	-13.61#06	٥	0,82562	(Eq. (15.114))	-	_	_	0.KS979	-1,65376				12R.46	Terrar day of the
Н. Ж7	2,13106	2.11106	3,4252	-15.75493	^	=	r	0.86359	-	-		0.75	you's			$\dagger$			100
														,			_	108.41	(propane)
15'.5'.57								<del></del>							15.63			110.49	112 (propana) 113.8 (butone)
																			Grabutana
H, J, D															15.63	_	<u> </u>	110,49	111.0 (butane)
Nahi																1	-		(Isobutane)
ZHC."H	2097[]	2.09711	3.4252	-15.75493	,	ī	I	0.86359	_	_	_	6.75	1.15796	•				100.50	108.6 (ncay: chloride)
																1	_	_	(acetome)
H, 2, 3															70.50	1	2	109.44	
دردر. دردرد	2,91547	2.91547	4.795R	-16.68412 C.	77	-16,65412	я	0,81549	0.81549	_	-	-	0.81549	SERVE I.	70.56	+	-	109.44	NO11
7. C.H	2 91547	211333	4.1633	.15.55033	5	-14.12375	-	0.87495	0.9(77)								-	i i	(isobutene)
אנ"כ"א	2.91547	202711	4.1633	-15.55033	-	-(4,13575					-		and a	P	T	+	=	110.76	
4.00						ı.	-	0,87493	0.91771	0.73	-	Q.75	1.04RR7	•			_	72111	111,4 (stobutane)
, ', II	2.90327	2.90327	4.7938	· · ·	,	2,523,52 	_	· 0.87495	17710,0	6.73	_	0.75	1,04RBIT	-1.45836		-	+		111.4
7.5.5										1							<u> </u>	<u> </u>	(usobutane)

NITRILES  $(C_n H_{2n-1} N, n = 2,3,4,5...\infty)$ 

The nitriles,  $C_n H_{2n-1} N$ , comprise a  $C \equiv N$  functional group, and the single bond of carbon to the nitrile carbon atom, C - CN, is also a functional group. The alkyl portion of the nitrile may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and 5 may comprise methylene  $(CH_2)$ , and methylpne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C - C bonds can be identified. The n-alkane C - C bond is the same as that of straight-chain alkanes. In addition, the C - C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C - C bonds comprise functional groups. The branched-chainalkane groups in nitriles are equivalent to those in branched-chain alkanes.

The nitrile  $C \equiv N$  is solved equivalently to acetylene as given in the Acetylene Molecule section except that the energy for  $\Delta E_{H_2MO}(AO/HO)$  is two times that given in Eq. (14.343), 16.20002 eV, in order to match the N AOs to that of the nitrile  $C2sp^3$  HO having a bond order 15 of three.  $E_T(atom-atom,msp^3.AO)$  of the  $C \equiv N$  functional group is  $-1.56513 \ eV$  (Eq. (14.342)) corresponding to the third-order bonded  $C2sp^3$  HO.

The C-CN functional group is equivalent to that of an alkyl C-C group given in the Continuous-Chain Alkanes section except that  $E_T(H,MO)$  and  $\overline{E}_{KWb}$  are those corresponding to a nitrile. As given in the Continuous-Chain Alkanes section,  $E_T(atom-atom,msp^3.AO)$  of the 20 alkyl C-C group is -1.85836~eV where both energy contributions are given by Eq. (14.513). It is based on energy matching within the nitrile. It corresponds to the maximum-magnitude energy contributions of a single-bonded and a third-order bonded  $C2sp^3$  HO.

The symbols of the functional groups of nitriles are given in Table 15.141. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of nitriles are given in Tables 15.142, 15.143, and 15.144, respectively. The total energy of each nitrile given in Table 15.139 was calculated as the sum over the integer multiple of each  $E_D(cirrup)$  of Table 15.144 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mog}$  that is subtracted from the weighted sum of the

 $E_D(G_{map})$  (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of nitriles determined using Eqs. (15.79-15.108) are given in Table 15.146. The C of the  $C \equiv N$  group can further bond with only one atom, and the bond is linear as a minimum of energy as in the case of acetylene and alkynes.

Table 15.141. The symbols of functional groups of nimites. Functional Group	furctional groups of nimites. Group Symbol
NOO	0-0
3	CIEN
CH, group	$C \sim H$ $(CH_3)$
CH1 group	C-H (CH,)
CH (alkyl) group	
CC bond (n-C)	(a)
CC bond (iso-C)	(a)
CC bond (tert-C)	(0)
CC (iso to iso-C)	( <del>)</del> ( <del>)</del> ( <del>)</del> ( <del>)</del> ( <del>)</del> ( <del>)</del> ( <del>)</del> ( <del>)</del>
(2101)	(e) ()-()
CC (t to iro-C)	(C) (C)

	) 2-2	dippo	· 2.1072	14516	2		1.53633		1 532	(propane	1.531	(butane		06/75.1	00000
	(a) 2-2	Comp	2.10725	1 45164	1.13101		1,53635		1.532	(propane)	1.531	(butanc)	03003	06126.1	000070
	(p) 2-2	donin	2.12499	1.45744			1.54280		1,532	(propane)	1.531	(butane)	1 5/5/5	1:0010	O KOKOO
	C-C (c)		2.10725	1.45164		_	1.53635		1.532	(propane)	1.531	(butane)	03263	2012011	O KRRRR
	C-C(b)		2.12499	1.45744			1.54280		1.532	(propane)	15.7	(milante)	1.54616		0.68600
	C-C(a) Group	2 12/00	4.16437	1.45744			1.54280		1.532	(propane)	157	(Oniging)	1.54616	20,000	0.08000
	C-H Group	1 67465		1.0360.1			1.11827			(icohutna)	Commonosia		1.29924	30000	0.00075
al values 11.	C-H(CH <sub>1</sub> )			Cecen.i			1,11713		1.107	1117	(C-H butane)		1.29569	05/1290	, , , , ,
I Salites all experimental values (	C-H(CH,)	1.64920	1,04056	70101		1.007.	1.109/4	1,00	(C. H. nomena)	1.117	(C - H butane)		1.4/20	0.63.580	
100000000000000000000000000000000000000	Group	1.20590	1 09811		_	1 14.231	17701		1.159	(acetonitrile)		0,000	0.47620	0.91064	
	C-C (i)	1.91255	1.38295			. 59697			1.468	(acctonitrile)		0310821	1120511	0.72309	
Т	rarameter	0 (0°)	c' (a.)		DONG	Length Hzg th	),sc.	Evn Band	Length	3	()	h.c.(a)	6	a	

Table 15.142, The geometrical bond parameters of nitriles

Table 15.143. The MO to HO intercept geometrical bond parameters of nitriles. R.R., R. are H or alkyl groups. E <sub>7</sub> is E <sub>7</sub> (atom – atom, nixp <sup>2</sup> .AO)	nerrical bon	nd parameters of	nimies. R.R.R.	" are # or alky	1 groups. C, 13	Cr (alom - ak	m, msp AU).								
Bond	Atom	£,	£,	Er	Ģ	Final Total	[,]	Ĩ	Comban	$E(C2xp^3)$	ю	-8	6	ď	9
		(eV) Bond 1	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	(7.2yp)	(°)	(°)	(eV) Final	(eV) Final	<u> </u>	©	C	(%)	(0)
RH;C,C, = N	×	-0,7K257	0	0	۰		0.930R4	0.87170	-15.60832		147.01	32.99	77.74	0.36699	0,73114
RH;C,C, = N	ڻن	-0.78257	-0.92918	0	0	-153,32744	17716.0	0.82272	-16.53750	-16.34664	145,42	34.58	95,00	0,42077	0,67736
RHich-C,N	ن	40,92918	-0.7#257	0	0	-133,32744	17710.0	0.82272	-16,53750	-16.34664	81.32	89'86	23.00	1,50718	0,1242
H,C, -C,N	ر.	-0.92918		0	0	-152.54487	17716.0	0.86359	-15.75493	-15.56407	85.50	94.50	10.67	1.45066	1,120.0
RH,C,H,C,C,N R=albyl	ر د	-0.9291R	41.92918	0	0	153,47406	12216'0	0,81549	-16.68412	-16.49335	80.53	73.00	37.51	1.51712	0.13423
$(c-H(CH_s))$	ر.	AICEOT-		С	0	-152.54487	14416'0	0.86359	-15,75493	-15.56407	77.49	102.51	41.48	1,23564	0,18708
( C - H (CH <sub>1</sub> )	ن	41626.0-	-0.9291R	0	0	501-71.	12216'0	0.81549	-15.61412	.16,49325	68.47	11.53	35,84	1.35486	0.29933
C-H (CH) (ii)	Ü.	-0.93918	-0.92918	#1626.D-	•	-154,40324	1,71171	0,77247	-17,61330	-17,42244	61.10	118.90	31.37	1.42988	0.37326
$H_iC_iC_iH_jCH_i$ ~ (C $-\underline{C}$ (a))	°.	-0.9291K	G	ď	0	LAPPS TS1-	17710.0	0.16359	-15.75493	-15.56407	63.82	116.18	30.08	1.83879	938106
#\$\cup\$C_K#\$CH_\cup\$ (C=C (a))	c,	41,9291K	#1 <i>626</i> .0-	c	0	-153,47406	12216.0	0.81549	-16.61412	.16.49325	\$6.41	123.59	26.06	1.90190	0.45117
(C-C, (h, C, -R')HCH, -	ڻ.	#IGG"	81026.0-	-0.92918	c	-154,40324	17719.0	T44TT.0	-17.61330	.17,42244	48.30	131.70	21.50	1.97162	0.51388
$R - H_1C_*(R' - H_1C_*)C_*(R' - H_1C_*)CH_1 - (C - C_1C_2)$	ر.	40,92918	-0.72457	-0.72457	-0.72457	-154.71860	0,91771	0.75119	-17,92866	917.73779	12.87	131.79	21.74	1,95734	0.505.0
$I_{KDC}G_{*}(H_{*}G_{*}-R^{*})HCH_{*} (G-G,G)$	٠ ر٠	-0.92918	40.9291H	81@Z0.0-	0	-154,40324	ונדועס	0.77247	-17.61330	-17.42244	48,30	131.70	21.50	1,97162	0.51388
$(R' - H_1C_2)C_1(R' - H_2C_2)CH_1 - (C' - C' (e))$	C.	-0.72457	-0.72457	-0.72457	-0.72457	-154.\$1329	17712.0	0.76765	-17.92866	917.73779	\$0.04	129.96	22.66	1.94462	0.49298
(erc,c,(H,C,-R)HCH,-(C,-C,0))	. C.	-0.72457	ж1626.0-	ж 1626'0-	-0	E9861 '751*	17716.0	0.78155	-17,40169	-17.21783	BL-TS	22.121	24.04	1.92443	0.47279
$isoC_*(R'-H_1C_*)C_*(R^*-H_1C_*)CH_1-$ (C-C'(f))	ر.	-0.72.157	-0.72457	18427.0.	48424,0-	-154.51399	17116,0	0.76763	-17.92xGA	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Parameters	10 0 0	C. C. C. C. C. C. C. C. C. C. C. C. C. C	1								
	Group	Group	CH's	* E	Groun	(a) (b) (c) (c) (d) (d) (d) (d) (d) (d) (d) (d) (d) (d	(a) (3-1)	(c) C-C (c)	(p)	(e)	() D-D
n,	_	-	-				1	dipolic	dranb	Cranb	Group
1				,	-	-		-	-	-	_
	>	0	7	-	0	0	0	0	0	0	c
$n_1$	٥	٥	0	0	٥	0	٥	0	6		
ť	0.5	0.5	0.75	0.75	0.75	0.5	0.5	2	30	, ,	
C.	-	  -	-	_	-	-	-	3	cal.	60	0.5
'5	-	-	-	. -	- -	- .	- -	-	-	-	-
,	1000		-	-	-	-	-	-	-	-	-
-	0.3177	0.91140	0.91771	0.91771	0.91771	0.91771	0.91771	17710	17719.0	0.91771	0.91771
	٥	-	٥	_	-	0	0	0	-	-	
3	2	0	-	-		7	2	2	2	2	,
ซ้า	0	0	3	2	-	0	0	0	c		
; ائ	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	20	>0	90
۲.	-	1	_	-	1	-	-	-	-		3
P, (aV)	-33.01231	-207.49229	-107,32728	-70,41425	-35.12015	-28 79214	A1021A	20 10113	7100.00	- 3	-
V, (cV)	9.83824	37.16984	38.92728	25.78002	12.87680	9.33352	9.33352	9 37773	P1757.07	71101.67-	-29.10112
T (eV)	8.63043	86.03250	32.53914	21.06675	10.48582	6 77464	6 77464	00000	200000	7.3/4/3	9.3/2/3
r, (e.P.)	-4.31522	-43.01625	-16.26957	-10,53337	-5.24291	-3.38732	-3 38712	1,45240	3 20727	6.90500	6.90500
E(10.10) (cV)	-14.63489	32,40004	-15,56407	-15.56407	-14,63489	-15.56407	-15 56407	16 35046	76/966	-3.43230	-3.45250
DEning (ar) (ar)	-1.85837	0	0		0	c	0	0.000	13,30407	-15.35946	-15.35946
Er (+0 10) (aV) .	-12.77652	32,40004	-15 \$6407	-15 56407	14.63.490	2017.4.51		5	0	0	0
E. (11,210) (0V)	.31 61537	71YU0 PG"	67 60461	40.55403	-14.03469	13.30407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
E (grom - grow men' 40) (av)	30301	25,30010	-07.09431	-49.66493	-31.63533	-31.63537	-31,63537	-31.63535	-31.63537	-31.63535	-31.63535
E (m) (an)	0.000.1-	-1.50513	٥	0	٥	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
2, (10) i.	-33.49374	-96.47124	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
to (10 rad s)	19.2516	22.0753	24.9286	24.2751	24,1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
7. (eV )	12.67172	14.53031	16,40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	100009	6 2003
n, (ar)	-0.23588	-0.24250	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	.0.20896	918810-	217710	0.174.6
$\mathcal{E}_{\text{tist}}\left(eV\right)$	0.11407	0,28107	0.35532 (Fa (13.458))	0.35532	0.35532	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312
E, (cV)	-0.17884	-0.10197	-0.22757	-0.14502	0.07200	0.10340	14	[5]	2	[2]	[2]
Em (cV)	0.14803	0.14185	0.14803	0.14803	0 14803	0.14803	0.14901	-0.15924	-0.10359	-0.10260	-0.10260
Er (Grap) (cV)	-33.67258	-96.77713	70/22/07	-49 R000K	11 70732	11 (022)	0.14003	0.14803	0.14803	0.14803	0.14803
Guard (s. 10'10) (cV)	-14.63489	-14.63489	-14.63489	-14 63489	14 63/20	.33.397.32	-33,49373	-33.24376	-33.59732	-33.18712	-33.18712
15,000 (a. 10 10) (a.V.)	0	0	-13.59844	-13 59844	11 40844	-14.03489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
E, (cmy) (dV)	4 40280	8 87504	70107 51	2000	13.27044		0	0	0	٥	0
		10000	12,42100	01000.	3.3.2001	4.32754	4.29921	3.97398	4.17951	3.62128	101724

	is subtracted from the weighted sum of the $E_D$ (see) (eV.)	
	that	
is calculated using the functional group composition and the energies of Table 15.144 compared in the group manual pathology.	State of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state	
a our cicigies of mitti	osition is given by (15.58	
1012111	values based on compe	

	Name	ひーン	() ひーン	C=N.	CH.	CH	15	((),)-()	1,0-0	(a) (b) (c) (c) (c) (c)	13							
		5	ę.	Group			:		٠ :	ن د	(2)	[]	(a) C – (c)	(a) U-U	23	Colculated	Experimental	Relative Error
Z,	Acetonitrile	-			-	9									•	Frem: (A)	Total Bond	
z z	Poparentrile			_	_	-		÷	c	<b>c</b> (		•	c	0	0	25,72040	25.77	PC1000
Z, 7, 0	2-Methylpropanerimie					<b>~</b> ;	c	7	· c					۰ ،	01	37.17830	7.72	0,00171
スチン	Pentanenitrile	-			7 -	۰,		5	7	c			: c		<b>.</b>	50,03600	50,0k	0.00002
Z	2.2-Dimethylpropanentrile	_			- ~	n =		ms	c (	0		_	. 6	۰ د	0	50,13689	æ ; S (	0.0002
2	Determinite				_	v.		'n		~ ~			c ·	0	• 🕆	62-17823	6 5 5	-0.00132
No. Hail	Decementinie					٠.	c	હ	٠.	0.0				۰ د	•	86.50910	K6.59	0.00000
Z T	Terradeconentrile	-				c 7	0 0	× 2	,c =	<b>c</b> c			0		. 0	122.9K220	58.75 57.85	0.00000
													-	0	c	171.61300	171.70	0.00052
2 Table 15.14	5 Table 15.146. The bond angle parameters of nitriles and experimental values [1].	neters of nitriles a	and experi-	mental value	3[1]. In the c	. In the calculation of $ heta$ , the parameters from the precedim source was $E : E \subseteq \mathbb{R}$	9. the paramet	ers from the r	receding an	nla syana syana		1	10, 1					
Atmin of Argic	(Argk 2c'	76.	14	-	A loan !	-			1111	noen arm arg	. Cr 15 Cr	arom – arom	.m.m. AC).					
			-			•	Alom 2				L							

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		Gal. 6	_		2	109.50	109,44	TT YU!	110.49		-	701	109.50	100.44	109.44			110,76	=	-
			_		L	H				_		-		_		L			_	
	-	<b>9</b> 3	_	_	L.	Н	26			_	_	_		2	9	_	_			
	-	<b>₽</b> , 3	_	_		Н	70.36		69.51		69 53			70.56	70.56		_			_
		ج رة م	( )			0		O			ı		0			-1,85836	,	=	0	
10.1	TAP. AO).	·~				1.15736		1.15796					1.15796			0.81549	tan d	l'oden'.	L.OHKK7	
-	m – alom, n	·-				6.75		Q.75					0.75			_	100		0,75	
7 12 15 15	1. 18 Cr (all	<i>;</i> -	_			-		-					-			-	-		-	
Past oren	rie useu.	<i>;</i> 	_			-		-					-			-	0.75		0.75	
eding pante	2	View 2				-		-					-			0.RT549	0.91771		0.01771	
from the pre-		Aben (			1	U.RRADS		(LRK359)					U.Kr.d.sy			0,X15.49	0.87495		CELTAUS	
e. the parameter	Atom 2	Hybridization Designation	Challe 16 9 43	10.000	3			=			-	-	-			ກ	-		-	
alculation of	E	Aloun 3										1	:		-16.68412	۲,	-14.82575	-14.82575	ر.	
The base angle parameters of minical and experimental values [1]. In the calculation of 9, the parameters from the preceding angle angle and the calculation of 9, the parameters from the preceding angle and the calculation of 9, the parameters from the preceding angle and the calculation of 9, the parameters from the preceding angle and the calculation of 9, the parameters from the preceding angle and the calculation of 9, the parameters from the preceding angle and the calculation of 9, the parameters from the preceding angle and the calculation of 9, the parameters from the preceding angle and the calculation of 9, the parameters from the parameters from the calculation of 9, the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from the parameters from	Alom	Designation	(Toble 15.3.A)		-		,					-				ກ	5		<b>~</b>	
xpcrmental	E contembre	Abta			-15.75403		-15.75403					.15.75493			-16,68412	<u>.</u> ئ	-15.55033 C.	-15,35(633	نځ	20077
numes and e	77.	Aberra (O <sub>0</sub> )			3.4252		3,4252					3,4253				4.793K	4,1633	+-	4,1633	
WINCIGES OF	. 5c.	(°)			209711		2,11106					202711				231344	211333		Trans	
and an Bure has	2c'	(%)			1,007		21106		-,.			11007			20,000	1	2.91547	2015/7	1011	
	Alers of Argic			Z,C,N	ZHC,H	*.)'.)#7	Makins LHC H		*,1'.'C,"		Z.L.,17	Meliti ZHC H	70,07	н'.5'.37	לכ'נ'נ'		#".)"37 % C" ()	H,''),'32	i i	70:0:07

THIOLS 
$$(C_n H_{2n+2} S_m, n=1,2,3,4,5...\infty)$$

The alkyl thiols,  $C_nH_{2n+2}S_m$ , comprise a SH functional group and a C-S functional group. The alkyl portion of the alkyl thiol may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2CH)$  and t-butyl  $((CH_3)_3C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in thiols are equivalent to those in branched-chain alkanes.

The parameters of the SH functional group is solved using Eq. (15.41). As in the case of the C-H bonds of  $CH_n$  n=1,2,3, the S-H-bond MO is a partial prolate spheroid in between the sulfur and hydrogen nuclei and is continuous with the S3p shell. The energy of the  $H_2$ -type ellipsoidal MO is matched to that of the S3p shell and comprises 75% of a  $H_2$ -type ellipsoidal MO in order to match potential, kinetic, and orbital energy relationships. Since the energy of S,  $E(S)=-10.36001\ eV$ , is less that that of H, the linear combination of the  $H_2$ -type ellipsoidal MO with the S3p shell further comprises an excess 50% charge-density donation from H to the S3p shell of the S-H-bond MO to achieve an energy minimum. The initial total energy of the shell is given by the sum over the four 3p electrons. From Eq. (15.12), the sum  $E_T(S,3p)$  of the energies of S,  $S^+$ ,  $S^{2+}$ , and  $S^{3+}$  [38] is

$$E_{T}(S,3p) = 10.36001 \ eV + 23.33788 \ eV + 34.79 \ eV + 47.222 \ eV$$

$$= 115.70989 \ eV$$
(15.118)

By considering that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{3p}$  of the S3p shell may be calculated from the Coulombic energy using Eqs. 25 (15.13) and (15.118):

$$r_{3p} = \sum_{q=12}^{15} \frac{(Z-q)e^2}{8\pi\varepsilon_0 \left(e115.70989 \ eV\right)} = \frac{10e^2}{8\pi\varepsilon_0 \left(e115.70989 \ eV\right)} = 1.17585a_0 \tag{15.119}$$

where Z=16 for sulfur. Using Eqs. (15.14) and (15.119), the Coulombic energy  $E_{Coulomb}(S,3p)$  of the outer electron of the S3p shell is

$$E_{Condomb}(S,3p) = \frac{-e^2}{8\pi\varepsilon_0 r_{3p}} = \frac{-e^2}{8\pi\varepsilon_0 1.17585a_0} = -11.57099 \ eV$$
 (15.120)

The sharing of the electrons between the S and H atoms permits the formation an S-H-bond MO that is lowered more in energy than the participating S3p orbital which consequently increases in energy. By considering the 50% electron redistribution in the S-H group as well as the fact that the central field decreases by an integer for each successive electron of the shell, the radius  $r_{S-H3p}$  of the S3p shell may be calculated from the Coulombic energy using Eq. (15.18)

$$r_{S-H3p} = \left(\sum_{n=12}^{15} (Z-n) + 0.25\right) \frac{e^2}{8\pi\varepsilon_0 \left(e115.70989 \ eV\right)}$$

$$= \frac{10.5e^2}{8\pi\varepsilon_0 \left(e115.70989 \ eV\right)}$$

$$= 1.23465a_0$$
(15.121)

where the s=-1 in Eq. (15.18) due to the charge donation from H to S. Using Eqs. (15.19) 10 and (15.121), the Coulombic energy  $E_{Coulomb}(S_{S-H},3p)$  of the outer electron of the S3p shell is

$$E_{Coulomb}(S_{S-H}, 3p) = \frac{-e^2}{8\pi\varepsilon_0 r_{S-H3p}}$$

$$= \frac{-e^2}{8\pi\varepsilon_0 1.23465a_0}$$

$$= -11.01999 \text{ eV}$$
(15.122)

Thus,  $E_r(S-H,3p)$ , the energy change of each S3p shell with the formation of the S-H-bond MO is given by the difference between Eq. (15.120) and Eq. (15.122):

$$E_{T}(S-H,3p) = E(S_{S-H},3p) - E(S,3p)$$

$$= -11.01999 \ eV - (-11.57099 \ eV)$$

$$= 0.55100 \ eV$$
(15.123)

15 Then, in Eq. (15.42):

$$E_{r}(AO/HO) = E(S) - E_{r}(S - H, 3p)$$

$$= -10.36001 \ eV - 0.55100 \ eV$$

$$= -10.91101 \ eV$$
(15.124)

And, in Eq. (15.56),

$$E_r(atom - atom, msp^3.AO) = 0.55100 \text{ eV}$$
 (15.125)

Due to the charge donation from H to S,  $c_1 = 1$  in both Eqs. (15.42) and (15.56). As in the case of the C - H-bond MO,  $C_1 = 0.75$  based on the orbital composition. In alkyl thiols, the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus,  $c_2$  in Eq. (15.52) is also one, and the energy matching condition is determined by the  $C_2$  parameter. Using the energy of S,  $E(S) = -10.36001 \, eV$  in Eq. (15.65), the hybridization factor  $C_2$  of Eq. (15.52) for the S - H-bond MO is

$$C_2(S3p \text{ to } H) = \frac{E(S, 3p)}{E(H)} = \frac{-10.36001 \text{ eV}}{-13.60580 \text{ eV}} = 0.76144$$
 (15.126)

Since the energy of S is matched to the Coulombic energy between the electron and proton of  $E(H(a_0))$ ,  $E_{initial}(c_{AO/HO}) = E(H(a_0)) = -13.60580 \ eV,$ 

- 10  $E_{initiol}(c, AOIHO) = E(H) = -13.59844 \ eV$ , and  $E_{mog}$  is that corresponding to  $E(H(a_0))$  given by Eq. (15.58).  $E_D(Group)$  for hydrogen sulfide is equivalent to that of the SH functional group, and the  $E_D(Group)$  (eV) for dihydrogen sulfide follows the same derivation as that for the SH functional group except that the parameters correspond to  $n_1 = 2$  rather than  $n_1 = 1$  in Eqs. (15.42) and (15.56).
- Furthermore, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the C-S-bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with E(AO/HO) = 0 and  $E_T(AO/HO) = \Delta E_{H_1,HO}(AO/HO)$ . Then, the solution of the C-S functional group comprises the hybridization of the 2s and 2p AOs of C to form a single  $2sp^3$  shell as an 20 energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the S AO to form a MO permits each participating orbital to decrease in radius and energy. Since the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243),  $c_2$  in Eq. (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. Then,  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a 25 corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), and the S AO has an energy of  $E(S) = -10.36001 \, eV$ . To meet the equipotential condition of the union of the

C-S  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.51) for the C-S-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO \text{ to S}\right) = \frac{E(S)}{E(C,2sp^3)}c_2\left(C2sp^3HO\right) = \frac{-10.36001 \text{ eV}}{-14.63489 \text{ eV}}(0.91771) = 0.64965 \quad (15.127)$$

Since the sulfur is energy matched to  $E(H(a_0))$  in the S-H-bond MO,  $E_T(atom-atom, msp^3.AO)$  of the C-S-bond MO in Eq. (15.52) due to the charge donation from the C and S atoms to the MO is -0.72457~eV corresponding to the energy contribution equivalent to that of a methyl group (Eq. (14.151)).

The symbols of the functional groups of branched-chain alkyl thiols are given in Table 15.147. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and 10 energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl thiols are given in Tables 15.148, 15.149, and 15.150, respectively. The total energy of each alkyl thiol given in Table 15.151 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.150 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(Group)$  (eV) values based on composition is given by Eq. (15.58). The C-C bonds to the HCSH group (one H bond to C) were each treated as an iso C-C bond. The C-C bonds to the CSH group (no H bonds to C) were each treated as a tert-butyl C-C.  $E_{mag}$  was subtracted for each t-butyl group. The bond angle parameters of alkyl thiols determined using Eqs. (15.79-15.108) are given in Table 15.152.

Table 15,147. The symbols	Table 15.147. The symbols of functional groups of alkyl thiols.
Functional Group	Group Symbol
SH group	153
H <sub>S</sub> S	H.S
S	ر د - د
CH <sub>3</sub> group	C-H (CH,)
CH <sub>3</sub> group	C-H (CH.)
H	; ;
CC bond (n-C)	(a) (j = ()
CC bond (iso-C)	(a) (j-)
CC bond (terr-C)	(a)
CC (iso to iso-C)	(E) (3-1)
CC(tro t-C)	(e) (j - j - j - j - j - j - j - j - j - j
CC (t to iso-C)	(E) U-U

	€) U-U	Group		2.10725		1.45164		1.53635		1.532	(propane)	1.531	Chattan		1.52750	24000
	(E)	Group		2.10725	13.55	1.45104	1000	1.53635		1.532	(propane)	1531	(butane)		1.52750	00000
4,00	(e)	6		2.12499	1 46744	A (CA)	1 64780	2074		1.532	(propane)	1.531	(butano)		1.54616	O 68600
(") (")	(A)	5	2 (000)	67/017	1 45164		1 53635			756.1	(propane)	1.531	(butane)		05/75.1	0.68888
C-C (b)	Choun		2 13400	2.12737	1.45744		1.54280		1637	760	(propane)	155.	(butane)	1 54515	01050	0.68600
C-C(a)	Group		2.17499		1.45744		1,54280		1 643	(annual)	(probatic)	7 (1)	(Durane)	1 54616	212	0.68500
L	Group		1.67465		1.03661		1.11827		1.107		(lenhintana)		İ	1,29924		0.03093
C-H (CH.)		Group	1.67122		5660.1	. 11713	1.11713					(C-H humane)	2000	1.29569	07630	0.03139
 C-H (CH,)	: model		07650	1 04055	06840.1		1,10974		701.	(C - H propane)	1.17	(C-H butane)	Jonah I	(67/7"	0.63580	20000
ς−ς	ag 5	25000	5/6061	171455	200		1,81460	0181	610.1	(methanethiol)			C1178 U	31115	82778	
HS O	diono	CATER 1	20100.1	1.26842			1,34244	1 34066		(hydrogen suffide)	7	(methanethiol)	13964		0.69025	
$S-H(H_2S)$		1.83767		1.26842		13000	174544		_	1.3356	_		1,32964		0.69025	
rarameter		0 (0,)		ر. د. (œ)	Dand I sand	influence conditions	2c' (A)	Exp. Bond		Central Central	3		b,c (a,)		ъ	

Table 15.149. The MO to HO intercept geometrical bond parameters of alkyl thiols. R. H. R. are H or alkyl groups. Er is Er (anna - anna, map'-AO)	netrical bon	d parameters of:	alky! thiols. R.,	Il. Il are H or	sikyl groups &	r is Er ann-	- onm, msp*.Ac	· o			i				
Bond	Atom	E,	E,	E,	1,1	Final Total	[]	3	Ender	. E(('2rp')	.0	6	9,	, d	d,
• .		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Energy C2sp <sup>2</sup>	(3)	(0)	Find	(es	ε	٥	€	(°)	(a)
						(§									
S-H (hydrogen sulfide) (dihydrogen sulfide)	×	0.55100	e				132019	1.23465	-11.01999		59'101	21.35	61.62	0.87355	0.39487
RS - H	,	-0.36229	0,55100	o	0		010281	0.92955	- 14,63704		67.09	1676	44.28	1,31557	0.04714
C, H3-SH	. 8	-0.36229	0,55100	0	0		010251	0.92955	-14,63704		132.06	47,94	55.13	1.09181	0.62274
C,H, -3H	.,	62206.13-	0	. 0	c	-151,97798	17716.0	0.89582	-15.18804	-14.99717	69.84	110.16	88.87	0.03762	1.67072
RC, H, C, H, - C, H, SH	٠	40,36229	4,92918	o .	ß	-152,90716	17716,0	0.84418	-16.11722	-15.92636	128.69	51.31	51.57	1.18689	0.52765
('-H ('H')		40.92918	0	0 .	o	1152,54487	12416.0	0.RG359	415.75493	-15.56407	67.77	16.201	41.48	1,23564	0.18708
C-H (CH;)		#1626.D	-0.9291#	. 0	o	-153,47406	12216'0	0,81549	-16.68412	-16,49325	68.47	11.33	33,84	เวราชด	0.20953
(H (c.H)	į	41.9291R	-0,92918	\$1626'0*	đ	154.40324	14416.0	0,777477	-17,61330	-17,42240	61.10	111.90	31.37	1,42988	0.37326
H,C,C,H,CH,	ن	#16\$6'U-	0	. 0	a	apps TSI-	17716.0	0.86359	-15.75493	-15,56407	CA.EA	116.18	30.08	1.83879	0.38106
H,C,C,H,CH2 (2)	C.	R1929.0-	stozo'o·	٥	a	-153.47406	17716.0	0,8154.0	-16.68412	-16.49325	38.41	123.39	20.05	1.90890	0.45117
$(R-H_sC_s(H_tC_s-R)HCH_s-IC_s-C_s(H_tC_s-R)HCH_s-IC_s$	<u>ئ</u>	*16Z670-	#16 <b>2</b> 6'0-	. 31626,0-	0	154,40324	12216'8	14577.0	-(7.61330	-17,42244	48,30	131.70	21.90	1.971@	0.51383
$R - H_2C_s(R^s - H_2C_s)C_s(R^s - H_2C_s)CH_2 - (C^s - C^s)$		#1626'0 <del>-</del>	L\$\&L'0-	1572.0-	15PEL'0-	-154,71860	17714,0	0,751470	-17.92866	617.17.11-	48.21	(31,79	21.74	1.95734	0.50570
(C - C' (H, C, - R')HCH; -	, C,	#10 <u>5</u> 0.0-	\$1626'0-	41626.0-	U	-154.40324	17716.0	14277.0	OKE19721-	-17,42244	4830	131.70	21.90	שוצפו	0.51388
$(R', (R'-H_3C_s)C_s(R'-H_3C_s)CH_1-(C'-C'(e))$	۲,	12427.0-	-0,72457	-0,72457	15121.0-	66157 <b>51</b> •	17718.0	0.76763	55826.71.	977.71-	\$0.04	76'621	2266	1.0462	0,49208
$(C_1 - C_1)$	: C.	-0.72457	-0.9291K	-0.9291R	·0	-154.19KG3	17416.0	0.78155	-17.40869	-17.21783	52.78	17.23	24.04	1,92443	0.47279
$ImC_{*}(R'-H_{2}C_{*})C_{*}(R'-H_{2}C_{*})CH_{2}-IC_{*}CC-C_{*}(f)$	:5	-0,72457	-0 72457	-0.72457	-0.72457	-154.51399	17716.0	0.76763	9982671-	-17.73779	\$0.04	96'671	22.66	1,04462	0.49298

Table 15.150. The energy parameters (eV) of fimetional groups of alkyl thiols.	cters (eV) of fimeti	chial proups of alky	vi thiols.									
Parameters	SτΉ	Sroup	S-3 Group	CH, Group	C'H <sub>z</sub> .	Oroup	Group	C-C (b) Group	(e) Croup	C-C (d) Group	C-C (e) Group	C-C (t) Group
n.	2	-	-	3	2	-		-	1	-	1	1
r.	0	0	0	2	-	0	0	0	0	0	0	0
u'	0	0	0	0	0	0	0	0	0	0	0	0
٢	0.75	0.75	0.5	6.75	0.75	0.75	5'0	5.0	0.5	0.5	0.5	0.5
	0.76144	0.76144	0,64965	-	-	-	1	_	1	1		1
is .	-	-	-	-		1	-	_	1	1	1	1
· ·	-	_	_	0.91771	17416.0	17716.0	17716.0	17719.0	17716.0	0.91771	0.91771	0.91771
ť	~	-	0	0	-	1	0	0	0	1	-	٥
	-	-	2	-	_	1	2	2	7	7	2	2
c c	-	-		3	2	-	0	0	0	0	0	Б
-	0.75	0.75	0.5	0.75	0.75	0.75	5.0	6.0	6.5	0.5	0.5	5.0
	0.76144	0.76144	0.64965	-	1	1	-	1	-	-	1	1
7 (a7)	-72.80662	-36,40331	-46,36495	-107.32728	-70,41425	-35.12015	-28.79214	128 79214	-29.10112	-28.79214	-29.10112	-29.10112
7, (27)	21.45310	10.72655	7.93551	38.92728	25.78002	12.87680	232252	9,35352	57.77.6.8	2388E-6	6.37273	9.37273
T' (aV)	19.81003	9.90502	12,13899	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V_ (uV)	-9.90502	4.95251	-6.06949	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3,38732	-3.45250	-3.45250
E(no no) (cV)	-20.72002	-10,36001	0	-15,56407	-13.56407	-14,63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15.35946
DEnger (er m) (eV)	1.10200	0.55100	-0.72457	0	0	0	0	0.	0	0	0	0
E, l. to not (cV)	-19.61802	-10.91101	0.72457	-15.56407	-15.56407	-14,63489	-15.56407	-15,56407	-15.35946	-15.56407	-15,35946	-15.35946
Erlund (cV)	-63.27052	-31,63526	-31.63537	-67.69451	-49.66493	-31.63533	-31,63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
Er (ann - atom, nigh' At) (eV)	002011	0.55100	-0.72457	0	· O	0	-1.85836	95858.1-	\$1644'1-	-1.85836	-1.44915	-1.44915
Er hal (cV)	-62.16874	-31.08437	-32,35994	-67.69450	-49,66493	-31,63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
ω (10 <sup>15</sup> roil 1s)	12.5415	12.5415	30.5436	24,9286	24.2751	24.1759	9.43699	9.43699	15.4846	9,43699	9.55643	9.55643
$\mathcal{E}_{\mathbf{r}}\left(eV\right)$ .	8.25504	8.25504	20,10434	16.40846	15.97831	15.91299	6.21159	65112'9	10.19220	6.21159	6.29021	6.29021
$\vec{E}_{p_i}(eV)$ .	-0.17669	-0.17669	-0.28705	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Pigmo (cP)	0.32422	0.33620	0.08146	(Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0,12312 [2]	0.17978	0,09944	0,12312	0.12512	0.12312
E (eV)	-0.01458	-0.00859	-0.24632	-0.22757	-0.14302	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E eng (cV)	0,11441	0.11441	0.14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Erland) (cV)	-31.10493 <sup>8</sup>	-31.09296	-32,60626	-67.92207	-49.80996	-31.70737	-33,59732	-33,49373	-33.24376	-33,59732	-33.18712	-33.18712
E (41. 10 110) (4V)	-13.60580	-13.60580	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	.14,63489	-14.63489	-14.63489	-14,63489	-14.63489
E (c. 10.11) (eV)	-13.59844	-13,59844	0	-13.59844	-13.59844	-13.59844	0	0	0	0	٥	0
Enlany (ar)	3.78628	5.77430	3,53648	12,49186	7.83016	3.32601	4,32754	4.29921	3.97398	4.17951	3.62128	3.91734
	1, 11 20001 25	11. 10000										

2 ( 1 1 . x . 1 , x ) = E (11, 1) - E, (11) = 62, 19789 eV - (-31.09296 eV).

Table 13.131. The total bond energies of alkyl thiols calculated using the functional group composition and the energies of Table 15.150 compared to the experimental values [3]. The magnetic energy E tast is subtracted from the weighted sum of the E (e-w) (eV) values base Composition is given by (15.58).

	1			,																						
	Relative Embr			001100	0.000	7000	10000	0.00003	0.00035	0.00003	0 0000		60000	O'DATAGO	D,00014	0.00012	PEUCO	0.000	2000	0.0003	·0.000%	110000	-0.00085	0.00143	0.00023	0.00020
	Experimental	Total Bond	Energy (eV)	250.5	202		227	31.762	43,933	44.020	56 (189	1×1 y)	701.77		563[3	68.314	68.264	179.89		200	GK.451	80.416	80,607	80.603	92.570	129.048
	Calculated	Tolal Bond	Energy (eV)	3.77430	7 56052		12.00204	31,76034	43.9.804	44.01.893	56.07574	1991 95	66 14720	200	1700Tuc	. 0090E'X9	68,23344	6K \$1707	62312.07	70000	68.5   797	\$039114	\$0.67567	80.71992	92.54584	129,02194
	E	ŀ		0	۰.			= 1	٥	c	0	0	c	, -	•	0	0	-	-	, -	7	•	÷	7	•	۰
	(J)			•	•	•			-	-	~		0			•	•	•	•			0	•	-	•	٥
	(e) U-U			=	•	c	-				•	5	0	•		-	•	0	•	•	•	5	-	0	0 -	٥
	C-C (q)			=	•	•	0		• •		•	0	•	-	•		٠.٠	0	-				2 6	، د		,
	(a) (-(a) (-(b) C-(c) (d)				٥.	=	c					۰.	•	m	•		۰ د	-	c	_			•	٠,	٠,٠	,
	(a)		9			•	0	c	,			7 .	۹.	0	••		• •		•	=	¢	: =		4 6	• •	
13.7	(g)		-		= =	2	-	~	c				= 1	0	_					_	~	. ~				
77.7	5		c	-	: 6	2 1	6	<b>c</b>	_	-				-	_	~			•	-	0		_			
7.7	Ë		=	-				~	c	m	_	_		•	~	-	_				•••	~	c	•	0	
n.)	ī.		-	•	-			-	~	_	7		-		•	_	m				-	•	7	_		
7	Group		•	0		_		-	-	_	-	_	_			-	-	-	-		-	_	-	-	-	
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×.	Group		- :	=	=	0		: =	- 1	-	-	c		_	: :	، د	-	~	-	-	- 4	0		ь.	۵	
		Hadronson Callida		בייני המלכם שהווכנ	Mediancibio	Ethanethiol	1-Pronamerhiol	2.Pronamelija			t-bulancuioi	4-Mathyl-I-propanethiol	2-Methyl-2-propanethiol	2-Mathri-1-butmerhiol	1. Beninneiliei	The factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of the factor of th	TANKER PERSONAL PROPERTY OF	- Wolland P-2-ballandhiol	2.2-Dimethyf-1-propanethiol	1-Hexanethiol	Market 2 nonlinearing	District of the second	Lancon Lancon Lancon Brechmon	The section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the section of the se	-Uccarionalol	
		H.	7		3	CHES	CHIS	S.H.S	7	2	3 .	2 0	3	ر الا	7			2.5	25	ž	C.F.		3	3	211111	

Table 15.132. The bond angle parameters of alkyl thiots and experimental values [1]. In the calculation of 8,, the parameters from the preceding

	<del></del>						_										
Exp. θ (•)	96.5 (methanchiol)	(cthanethiol)	(etherethiol)	(propane) 112 (propane) 113.8 (butane)	(Tobelane)	(Puttane)	(ixplutane)				(isolations)			(isobutane)	7111	(isobutane)	
(a), B.	97.28	8 97	ă	110.49		110,49		109.50	109,44	100.44	10.67		9,79	72,111		47	47.50
. C								_							T		r
e_ ⊙																	
0, ©	_	_	_	1569		(9,51	$\perp$		70.56	70.56							72.50
E <sub>r</sub> (6V)	e	-0.72457	٥			,					-1.85836			o	A5030 1.	New'i.	
<b>.</b>	L.GAIS	0.7337	1.15736					1.137%			0.HI549	1.04887		1,04897	) Outer		
£ .	0.75		0.75					C/'n			-	0.75		0.75	0.73		
ሪ <sup>•</sup>	-	0.64763 (Eq. (15.127)	-				-	-			-	-		-	_		
<del>ن</del>	0.73	_	-				-	•			-	0.75		0.75	27.0		
C,	0,86359	0,64963 (Eq.(15,127))	-				-				Q.81549	0.91771		111111	17716-0		
<b>្</b> រុំ	Q.76144 (Eq. 13.(25))	0,81349	0,16339				O.RAGESIJ		1		0.R[540	0,87495		CCP IN'T	0,87495	1	
Hybridization Dosignation (Table	v	, s	=				×				a	-	-		-		
Arms 2	-15.75493	-10,36001 S	×				Ξ			-16,68412	ن	-14833	-14.82575	Ų.	-14.12373		
Hybridization Designation (Table 153.A)	4	ก	7				,				q	•	3		. ~		
Am i	. 100,34,001	-16,68412 C.	-15.75493				-15.75493			-166412	ن	., .,	-13.55033		-13,2033		1
Transied Annus ( a, )	73166	\$.2344	34332				3.4252			agus P		4.1633	4,1633	- 1	4.7958		
: <u>]</u> .g	3,42910	3,42910	2.11106				2.09714			201647		2,11323	2.09711		2,90327		
] g	2,53685	2,91547	2.11106				2.09711			291547		2,91547	291547		2,90327		
		N".J".37	н. энг	לנ"נ"ני		H'5".17	ZHC, H	7,7,7,7	H'5":37	75.5.77	7.0.7	, , , , , , ,	H', J', 17	70.00	· · · · ·	*.j'.j'.j*	

SULFIDES  $(C_n H_{2n+2} S_m, n = 2,3,4,5...\infty)$ 

The alkyl sulfides,  $C_n H_{2n+2} S_m$ , comprise two types of C-S functional groups, one for t-butyl groups corresponding to the C and the other for the remaining general alkyl groups including methyl. The alkyl portion of the alkyl sulfide may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in sulfides are equivalent to those in branched-chain alkanes.

Each C-S group is solved by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the S AO to form a MO permits each participating orbital to decrease in radius and energy. Since the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243),  $c_2$  in Eq. (15.52) is one, and the energy matching condition is determined by the  $C_2$  parameter. As in the case of thiols,  $C_2$  of Eq. (15.52) for the C-S-bond MO given by Eq. (15.127) is  $C_2(C2sp^3HO to S) = 0.64965$ .

The C-S group of alkyl sulfides is equivalent to that of thiols where  $E_T(atom-atom, msp^3.AO)$  is  $-0.72457 \, eV$  (Eq. (14.151)). The t-butyl-C-S group is also equivalent to that of thiols except that the energy parameters corresponding to the oscillation in the transition state are matched to those of the t-butyl group.

The symbols of the functional groups of branched-chain alkyl sulfides are given in Table 15.153. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfides are given in Tables 15.154, 15.155, and 15.156, respectively. Consider that the C-S bond is along the x axis in the xy-plane. The S nucleus is at the focus +c and the C nucleus is at the focus -c. The elliptic angle  $\theta$ ' is taken as counterclockwise from the x-axis for S and as clockwise from the -x-axis for C. The total energy of each alkyl sulfide given in Table 15.157 was calculated as the sum

over the integer multiple of each  $E_D(G_{mup})$  of Table 15.156 corresponding to functional-group composition of the molecule.  $E_{mog}$  given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of alkyl sulfides determined using Eqs. (15.79-15.108) are given in Table 15.158.

CH, group	. — H (r.H.)
CH, group	C-H (CH;)
£	<i>H</i> −.0
CC band (n-C)	C-C (s)
CC band (iso-C)	( <del>Q</del> ) ::-:
CC band (tert-C)	ن-ن (ف)
CC (fan to iso-C)	(a)
CC (rint-C)	د. – د. (۵)
CC (t to iso-C)	C-C(0)
Table 15.134. The geometrical bon	Table 15.134. The geometrical bond parameters of alkyl sulfides and experimental values [1].

Group	2.10725	1,45164	1,53635	1,532 (propane) 1,531 (butane)	1.52750	0.68888
Group	2.10725	1,45164	1.53635	1.532 (propane) 1.531 (butane)	1.52750	0.68888
Group	2.12499	1.45744	1.54280	1.532 (propane) 1.531 (hutane)	1.54616	0.68600
Group	2.10725	1,45164	1.53635	1.532 (propane) 1.531 (butane)	1.52750	0.68888
Group	2.12499	1.45744	1.54280	1.532 (propane) 1.531 (butane)	1,54616	0.68600
Cre('(a) Group	2.12499	1.45744	1.54280	1.532 (propane) 1.531 (butane)	1.54616	0.68600
Group	1.67465	1.05661	1.11827	1,122 (isobutane)	1.29924	0.63095
C-H (CH <sub>2</sub> )	1,67122	1.05553	1,11713	1,107 (C-H propans) 1,117 (C-H butane)	1,29569	0.63159
C-H (CH,)	1.64920	1.04856	1.10974	1,107 (C-H propane) 1,117 (C-H butane)	1.27295	0.63580
C - S (ii) Group	1.90975	1,71455	1,81460	1,807 (dimethyl sulfide) 1,813 (ethyl methyl sulfide, avg.)	0.84112	0.89778
C-S(i) Group	1.90973	1.71455	1.8 1460	1.807 (dimethyl sulfide) 1.813 (ethyl methyl sulfide, avg.)	0.84112	0.89778
Parameter	0 (0,)	c. (a,	Bond Length 2c' (A)	Exp. Bond Length	b.c (a,)	

Bond			1			the designation of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of	-	·lan							
		/i, (e.V) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	Final Total Energy (72sp²	<u>(</u> ]E	'j <u>,</u> e,	Eradas (cV) Final	$E(c:2xp^2)$ (eV) Final	.e) (e)	, (°)	ς (•)	(°)	(0)
R-S-R ((''S (i) and (ii))	×	-4,36229	-0.34729		0		1,32010	0.87405	-15.55033		129.96	50.04	52.88	1.15262	0.56193
$H_1C_a = S = C_bH_1CH_2H$ $(C = S_1(0))$	ŗ,	-0.36229	ŋ	0	ø	19779.121-	17716.0	0.89582	-13,14404	-14.99717	130.79	49.21	53.75	1,12937	0.51518
$H_3C_a = S = C_bH_1CH_2R$ (C = N(1))	U	436229	-0 9201ж	o	0	-152 90716	17719,0	0.84418	-14.11722	-13.92636	128.69	15.18	51.57	1.18689	0.52765
$H_{r,C_{r}} = S = C_{r}(CH_{s})_{s}$ $(C = S_{r}(i) \text{ and } (ii))$	Ü	-0.36229	-0 72457	-0.72457	-0.72457	-154,15170	17716.0	0.78367	-17.36.74	-17,17090	125.97	24.03	48,94	1,25430	0.46025
('-H ('H,)	٤	#1626.0-	-	0	0	-152.54487	12216.0	0.86359	-15,75493	-15.56407	77.49	102.51	41.48	1,23564	0 18708
$C = H(CH_2)$	ن	-0,92918	-0.92918	0	0	-153,47406	0,91771	0,81549	-16.68412	-16.49325	68.47	11.53	35.14	13500	£1000 U
C11 (CH)	ü	*1626.0-	-0.9291R	K1626'D-	•	-154,40324	17716.0	0.77247	-17,61330	-17,42244	61.10	881	11.1		
H,C,C,H,CH, - (C'-C'(a))	۲,	#16Z6'0-	c	0	o	-152.54487	0.91771	0,16359	-15.75493	-15,36407	28.50	116.18	30.0%	1,83879	0.38106
$H_3(C, H_2(H_3 - (C - C, (a)))$	15	#16ZG'0-	81626'D-	С	0	-153,47406	0.91771	0,81549	-16,67412	-16,49335	56.41	123.59	26.06	068061	0.44117
((c,-(, (p)))   u-H-C,(C,(H-C,-R))HCH-=	ť	-0.92918	-0.92918	-0.9291я	c	-154,40324	0.9177	0.77247	-17,61330	-17,42244	48.30	131.70	21.90	291261	0 51388
(C - C, (C))	ئ	N1050.0.	-0.72457	-0.72457	-0,72457	-134.71800	0,91771	0.75829	-17,92866	617.73.79	4831	131.79	31.74	1.95734	0.30570
$ker(f_{\mathcal{L}}(H_{\mathcal{L}'}-H)HCH_2-f_{\mathcal{L}'}-f_{\mathcal{L}}(H_2)$	ڻ	*10 <u>70,</u> 0.	-0.92918	-0.92918	c	. 154,40324	0.91771	0.77247	-17.6(330	17,42244	4830	131.70	21.50	1.97162	0.51388
$(C-C, (R-H_2C_2)C_1(R-H_2C_2)CH_2-(C-C, (e))$	ڻ	-0.72457	-0.72457	-0.72457	-0.72457	-154.51399	0.91771	0.76765	-17.92866	617.73.719	50.04	12.96	22.66	1.94462	0.4929x
(נ'-(' (חָל', - א') אנ'איַ - (' (חָל', - א') אנ'איַ -	ť,	-0.72457	4,92918	R1620 0-	đ	-154.19863	17116.0	0.74155	-17,40869	-17,21783	32.78	17.71	24.04	1.02443	0.47279
$(RH_{2}(R-H_{2}C_{2})C_{3}(R-H_{2}C_{2})CH_{3}-(C-C_{2}(0))$	ڻ	-0.72457	-0 72457	-0.72457	-0.72457	-154.51399	17716.0	0.76763	.17.928GG	פתנת.וו.	30.02	129.96	22.66	1 DAMG	0.49298

ie 15.155. The MO to HO intercept geometrical bond parameters of aikyl sulfides. H.K.R. are H or alkyl groups. Et, is Et, (anni - atom, nityl. AO).

Table 15.156. The energy parameters (eV) of functional groups of alkyl sulfides.	ers (eV) of function	nal groups of alky	i sulfides.								
Parameters	C-5 (i)	C_5 (ii)	(H)	₹	C-#	C-C (a)	C-C (B)	(a) (b) (c)	(g) C-C (g)	(e) (J-(c)	(E) 13-13
	Group	Group	Group	Group	dness	dnero	dnoso	Group	dnoib	dioni	danio
r.	-	-	2	2 .	į	1	1	-	-	-	-
n,	0	0	2	-	Q	0	0	0	0	0	0
",	0	o	0	0	0	0	0	0	0	0	0
	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
13	0.64965	0.64965	_	-	1	-	1	1	1	1	1
2	-	-	-	-		-	-	1	-	1	1
	-	-	17710	17710.0	0.91771	0.91771	17716.0	0.91771	0.91771	0.91771	17716.0
6,	°	0	0	1	-	0	0	0	1	1	O
6,	2	2	-	-		2	2	2	2	2	2
25	0	0	3	2	-	0	0	0	0	0	O
	0.5	0.5	0.75	52.0	0.75	0.5	5.0	0.5	0.5	0.5	0.5
	0.64965	0.64965	-	-	-	-	-	1	1	1	1
r, (cr)	-46,36495	-46.36495	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (aV)	7.93551	7.93551	38,92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	12.13899	12.13899	32,53914	21.06675	10.48582	6.77464	6.77464	00506'9	6.77464	6.90500	6.90500
V, (aV)	-6.06949	-6.06949	-16.26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
15 (no im) (eV)	0	0	-15.56407	-15.56407	-14.63489	-15,56407	-15,56407	-15.35946	-15.56407	-15.35946	-15.35946
ΔΕ <sub>11,10</sub> (w m) (cV)	-0.72457	-0.72457	0	0	0	0	0	0	0	٥	٥
Er (40 10) (cV)	0.72457	0.72457	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
Er (n,m) (aV)	-31.63537	-31.63537	-67.69451	-49.66493	-31,63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_r(atom - atom, msp^3, AO)$ (eV)	-0.72457	-0.72457	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
Er(10) (cV)	-32,35994	-32.35994	-67,69450	-49.65493	-31,63537	-33.49373	-33.49373	-33.08452	-33,49373	-33.08452	-33.08452
ω (10 <sup>13</sup> rad/»)	30,5436	8.92777	24.9286	24,2751	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
$\mathcal{E}_{\kappa}(aV)$	20,10434	5.87641	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
E, (aV)	-0.28705	-0.15519	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
$\vec{E}_{kors}$ (cV)	0.08146	0.08146	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312 [2]	0.17978	0.09944 [5]	0.12312 [2]	0.12312	0.12312
E_ (aV)	-0,24632	-0.11446	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
Esur (cV)	. 0.14803	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Er (inne) (cl/)	32,60626	-32,47440	-67.92207	-49,80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
Executor to 10) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489
Estate (r. 10 10) (cV)	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
Entray (aV)	3,33648	3.20462	12.49186	7.83016	3.32601	4:32754	4.29921	3.97398	4.17951	3.62128	3,91754.

Table 15.157. The total bond energies of alkyl sulfides calculated using the functional group composition and the energies of Table 15.156 compared to the experimental values [3]. The magnetic energy 6, that is subtracted from the weighted sum of the  $E_{\mu}(\omega_{ms})$  (cV) values based on composition is given by (15.58).

		ב ב ב	(=) (=) (=)	:		3	(E)	( <u>e</u> )	C-C (a) C-C (b) C-C (c)	( <del>Q</del> )	(a) (b) (c) (c) (c)	9 5-5		Part Part		2
		Group	Group	:	•						2		2	Total Bond	Total Bond	Kelative Error
C;H,S	Dimethyl sulfide	2	0	7										Energy (eV)	Energy (eV)	
,H <sub>s</sub> S	Ethyl methyl sulfide	_		. ~	i <b>-</b>				0 1	ь.	•	0		31,65668	31.672	0.00048
His	Diethyl sulfide	~	•	. ~		•			0 (		0	•	0	43.81438	43,848	0.00078
H, S	Methyl propyi sulfide	74	•	. ~				- «	٥.	•	0	•	0	55.97208	56.043	0.00126
Z,H,	Isopropyl methyl suffide	7	•				• •	۰ د	۰ د	<b>5</b> (	•	•	0	55.97203	56.029	0.00102
Hrss	Butyl mediyl sulfide	2	0	. 74	:	- د	) r	• •				•	0	56.07297	\$6.115	0.00075
N.Y	t-Butyl methyl sulfide	-	-	4			• •		۰ د	0 1	0	۰	0	68.12978	68.185	0.00081
N,H	Ethyl propyl sulfide	-	0	7					٦,	<b>5</b>	0	0	7	68.28245	68.331	0.00
Y <sub>1</sub> ,S	Ethyl isopropy) sulfide	7	•		. ~	<b>-</b>	٠.	۰ ،	٠.	•	0	0	0	68.12978	68,210	0,00117
H''S	Disapropyl sulfide	~	0	•			- c	۷.	<b>.</b>		0	0	۰	68,23067	68,350	0.00174
H <sub>11</sub> S	Butyl ethyl suffide	~	٥	7	. 4	10		7 (	> 0		0	•	0	80,48926	80.542	0.00065
STIF	Methyl pontyl sulfide	7	0	2	. 4				2 0	۰.	0	0	0	80,28748	80,395	0.00133
Z .	Dibutyl sulfide	~	٥	٠,	ve	· c			> 0	<b>&gt;</b> (	0	0	0	80,28748	80,332	0.00056
His	Di-sec-butyl sulfids	2	•	-	. ~		<b>,</b>	•		<b>.</b>	0	•	0	104.60288	104,701	0.00094
٦ <u>.</u>	Di-t-buryl suffide	•	7	•			• c			<b>.</b>	ь.	•	٥	104,80456	104.701	-0.00059
H,5	Diisobutyl sulfide	2	٥	4	, , ~	۰,	•	> 4	٥ ٥	<b>.</b>	0	0	7	104,90122	104,920	0.0001
SEL	Dipontyl sulfide	۲,	0	~		• =	o o		= 6			0	•	104,74800	104,834	0,00082
H.S	Disonatví sulfida	•	•		,	•	•	>	5		c	•	•			

											_					
	Бър. в (•)		99,05 (dimethyl sulfide)	97 (ethyi methyi sulfide)	1)4.0 (ethyl methyl sulfide)	107 (propane)		111.0 (bume) 111.4 (isobume)	ing.3 . (dimethyl sulfide) i 10 (erhyl methyl sulfide)			11Q8 (isobutane)		111.4 (isabutane)	f11.4 (Gobutane)	
	Cal. 9 (°)		99.06	97.04	114.27	103.44	110.49	110.49	109.50	103.44	109.44	110.57	110.76	111.27	111.27	107.50
	92	- 1														
	10															
	o, ©					.	69.51	15.69		70.56	70.56					72.50
.msp .AO .	<i>Ε</i> <sub>τ</sub> (e <sub>Y</sub> )	. }	-1.85836	-1.83836	-0.72457	0 .			D			-1.15136	0	0	-1.83836	
агот – агот	<sup>‡</sup> 5		0,84418	0.83954	0.74282	1.15756			1.15796			67818.0	1.04887	1.04887	1,04887	
Er is Cr(	· u -		~	· ~ .	-	0.75	, ,	<u> </u>	8.0			-	6,75	0.75	6.75	
were used.	Ç,		-	-	0.64965 (Eq. (15.127)	1			-			1		ı	ı	
ding angle	Ç.		1	1		1			-			1	0,75	0.75	0.75	
from the prece	C, Aem 2		0.84418	0.81549	009180	-	-		-			0.81549	17719.0	17716.0	12216.0	
e parameters	C <sub>2</sub>		0.84418	0,86359	0.64965 (Eq. (15.127))	0.86359			0.86359			0,81549	501/8'0	\$6718'0	0,87495	
lculation of 0,, th	Atom 2 Hybridization	(Table 153.A)	11	. 25	. \$1	Ħ			ж			23	-	-	-	
I]. In the Ca	Economic Abres 2		-16.11722	-16 684) 2 methylens C,	-16.27490	π.			. 1			-16 68412 C,	-14,82575 C <sub>k</sub>	-14.82575 C.	-14.82575 C.	
rimental values [	Atora I Hybridization	(Table 15.3.A)	11	٢	s	۲			-			22	~	~	Ψ.	
tes and expe	E'imbooke		-16.11722	-15.75493 methyl C.	-10.36001	-15.75493			-15.75493			-16.68412	-15,35033	-15.55033 C <sub>5</sub>	-15,55033 C <sub>6</sub>	
alkyl sulfic	2c' Tentinal		5.2173	5,1381	5.3364	3,4252			3.4252			4.795	4.1633	4.1633	4,7958	
rameters of	2c' Bond 1	ું ક	3,42010	3,42910	291547	211106			200711			201547	211323	1,00711	2,90327	
nd angle pa	, 52°,	, ,	3,42910	3,42910	3.42910	211106			10021			2.91547	2.91547	2.91547	2.90327	
Table 15.158. The bond angle parameters of alkyl sulfides and experimental values [1]. In the calculation of $\theta_s$ , the parameters from the preceding angle were used. $E_p$ is $G_p$ (arom—aron, map40).	Metter of Angle		2C,8C,	2C, XC, (C: -S (i))	C:-S (ii)	Medichon ZHC, H	אנ"נ"נ"	H'5'.37	Mathy LHC, H	7,5,57	H".5".)7	70,00,00 in 0,	7,5°2,4 m.C,	#'5'57 ₩ 5''	امع ن' 20°ر'ر'	70,0,0

DISULFIDES  $(C_n H_{2n+2} S_{2n}, n = 2,3,4,5...\infty)$ 

The alkyl disulfides,  $C_nH_{2n+2}S_{2m}$ , comprise C-S and S-S functional groups. The alkyl portion of the alkyl disulfide may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in disulfides are equivalent to those in branched-chain alkanes.

Each C-S group is equivalent to that of general alkyl sulfides given in the corresponding section. As in the case of thiols and sulfides,  $C_2$  of Eq. (15.52) for the C-S-bond MO given by Eq. (15.127) is  $C_2(C2sp^3HO\ to\ S)=0.64965$  and 15  $E_T(atom-atom,msp^3.AO)$  is  $-0.72457\ eV$  (Eq. (14.151)).

The S-S group is solved as an  $H_2$ -type-ellipsoidal-MO that is energy matched to the energy of sulfur,  $E(S) = -10.36001 \ eV$ , such that  $E(AO/HO) = -10.36001 \ eV$  in Eq. (15.42) with  $E_T(AO/HO) = E(AO/HO)$ . The S-S-bond MO is further energy matched to the  $C2sp^3$  HO of the C-S-bond MO.  $C_2$  of Eq. (15.52) for the S-S-bond MO given by Eq. (15.127) is also  $C_2(C2sp^3HO\ to\ S) = 0.64965$ . In order to match  $E_T(atom-atom,msp^3.AO)$  of the C-S group  $(-0.72457\ eV)$  (Eq. (14.151)),  $E_T(atom-atom,msp^3.AO)$  of the S-S-bond MO is determined using a linear combination of the AOs corresponding to  $-0.72457\ eV$  and  $0\ eV$  in Eq. (15.29), Eq. (15.31), and Eqs. (15.19-15.20). The result corresponding to bond order 1/2I in Table 15.2 is  $E_T(atom-atom,msp^3.AO) = -0.36229\ eV$ .

The symbols of the functional groups of branched-chain alkyl disulfides are given in Table 15.159. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl disulfides are given in Tables 15.160, 15.161, and 15.162, respectively. The total energy of each alkyl disulfide given

in Table 15.163 was calculated as the sum over the integer multiple of each  $E_D(G_{mnp})$  of Table 15.162 corresponding to functional-group composition of the molecule.  $E_{mag}$  given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of alkyl disulfides determined using Eqs. (15.79-15.108) are given in Table 15.164.

Functional Group	Group Symbol
	CS
8-8	5-5
CH, group	$C = H \left( CH_3 \right)$
CH, group	$C-H(CH_s)$
5	<i>H</i> −.3
CC bond (n-C)	(; - (, (a)
CC bond (iso-C)	(e) U=U
CC bond (tert-C)	. (a) J=J
CC (iso to iso-C)	(p) U-U
(C101)	(a) U-U
C (to iso-C)	(S) U= U

able 15,160	ble 15,160. The geometrical band parar	trameters of alkyl disulfides and experimental values [1]	d experimental value	es [1].							
Brameter	ı	5-5	(H.) H-)	C-H (CH.)	C-H	(v) ))-)	(4) 2-2	(e) :)—:)	(p) 2-2	(e) <u></u>	(i) 2-2
_	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group	Group
0 (0,)	1.90975	2.37175	1.64920	1.67122	1.67465	2.12499	2,12499	2.10725	2.12499	2.10725	2.10725
c. (o°)	1,71455	0,91070	1.04856	1.05553	1.05661	1.45744	1.45744	1,45164	1.45744	1.45164	1,45164
Bond Length 2c' (A)	1.81460	2.02220	1.10974	61711,1	1,11827	1.54280	.1.54280	1.53635	1.54280	1.53635	1.53635
xp. Bond Length	1.816 (dimethyl disulfide)	2.029 (dinchyl disulfate)	1.107 (C-H propans) 1.117 (C-H butane)	1.107 (C - H propane) 1.117 (C - H burane)	1.122 ((sobutane)	1.532 (propens) 1.531 (butine)	1,532 (propene) 1,531 (butene)	1.532 (propano) 1.531 (butane)	1.532 (propane) 1.531 (butane)	1,532 (propane) 1,531 (butane)	1.532 (propane) 1.531 (butane)
b,c (a,)	0.84112	1,40510	1.27295	1.29569	1.29924	9194511	1.54616	1,52750	1.54616	1.52750	1.52750
	0.89778	0.80562	0.63580	0.63159	0.63095	0.68600	0.68600	0.68888	0.68600	0,68888	0.68888

		. S	- F	4	, E,	Final Total	3	,3	Erndon	E(C2sp')	.0	6	9,	d.	6
	-	Bond 1	Bond 2	Bond 3	Bond 4	dr.	<u>o</u>	(a.)	First)	(eV) Final	ε	ε	·©	ં	(a)
RS – SR (C – N (i) and (ii))	×	-0.36229	-0.18114	۰	e		1,32010	0.81527	11935 21-		i		1		
H,C, - SS - C, H, CH, R	-	-0.36229									27.5	67.63	31,93	1.84513	0,06558
H,C, - SS - C, H, CH, R					,	KUNE ICI-	0.91771	0.89582	-15.18804	-14.99717	130.79	19.21	53.75	1:12937	0.58518
(c x (0)	:	-0.36229	-0.929f#		۰	-152,90716	17710.0	0.84418	-16.11722	-15.92636	121,69	15.18	\$1.57	(,18619	0 17765
	ن	-0.36229	-0.72457	15127.0	-0.72457	-154.15170	0.91771	0.78367	-17.36176	17 17090	134.07	873			
. ·· - H (CH,)	ມ	-0.92918			٥	-152.544K7	0.91771	0.86359	197421-	15 56407	2 2	50.8	P(C) 12	1.25430	0.46025
$C = H \left( CH_2 \right)$	ن	11620'0-	-CL92918	0	0	153.47406	144190	A B S CAR	1			Can	46,14	1,2554	0,18708
(H (rH)	٦	.0.9291x	-0.92918	¥1626.0-	٥	PCAUP P\$ 1	14100	,,,,,,	71	10.477.2	68.47	111.53	35.6	135486	0.20933
H,C,C,H,CH, -	:								Uselin./i-	17.42244	61.10	118.90	31.37	1,42988	0,37326
(('-(: (a))	٠,	#1622.0-		0		-152.54487	17116.0	0.4K359	-13.75493	15.56407	63.82	116.18	30.03	1.83879	0.3X106
(( (. (a))	نځ	#1626.0-	-0.92918	۰	•	-153,47406	17416.0	0.81549	-16.68412	-16.49325	36.41	123.59	, ye ye	0000	
$R - H_1C_sC_s(H_1C_s - H^s)HCH_1 -$		81079 A.	2,000,0	0.000									array	Coreson	0.45117
(((. b))	-		16.62	816767-	c	-154.40324	0.91771	6.77267	-17,6(330	-17.42244	8.3	131,70	21.90	1.971@	315150
$K = H_1^{-1}(K - H_1^{-1})C_1(K - H_2^{-1})C_1$	ن	4.9291K	-0,72457	A.72457	-0 72457	154,71160	17716.0	0.75KBD	-17.72866	-17.73779	41.21	131.79	21.74	P.2561	01303.0
$IsM'', C', (H_3C', -R')HCH_3 - (C'-C', (d))$	ť	ж1,929,1%	-0.9291#	-0.9291K	c	-154.40324	17716.0	0.77247	-17.61330	-17,42244	8.30	02,70	8 5	9	
$(C-C, (R'-H_3C_s)C, (R'-H_3C_s)CH_3-(C-C, (e))$	5	-0.72457	.0.72457	-0,72457	-0.72457	-[54.5]399	1,7716.0	0,76763	-17.92856	-(1,73779	\$0.0k	129.56	32	978	
tanC,C,(H,C, - N')HCH2 - ((C - C (f))	ť	-0,72457	-0.92918	-0,92918	ć	-154.19263	17716.0	0,78155	-17.40169	MI 1771.	, i				Wassen T.
" " " " " " " " " " " " " " " " " " "		111111	!										5.	1.92443	0.47279
(C-C (D)	:	-0.72457	-0.72457	-0.72457	-0.72457	-134 51399	17716,0	0.76765	-17.92866	-17.73779	2005	129.96	22.66	1.94462	Q.4929R
										•		•		•	

Group Group Group	C-S()	S-S Group	C'H,	Group	Group	ر – در (a) Group	رام) (کامل	(c) Group	C-C (d) Group	C-C (e)	() C-C
n,	-	-	2	2	-	-	-	-	-	-	-
n,	0	0	2	-	0	0	0	c	c		-   -
n,	0	۰	٥	. 0	0	0	0		0	,	,
	0.5	0.5	0.75	0.75	0.75	5 0	6		,		, ;
	0.64965	0.64965	-	-	-		3	3	3	20	co o
,	-	-		- -		-	-	-	-	_	-
	-	-	-		-	-	-	-	1	1	-
5	-	-	0.91771	17116.0	0.91771	0.91771	0.91771	0.91778	0.91771	0.91771	17710
C <sub>3</sub>	٥	С	0	-		0	0	0	_	-	
5	2	2	-	_	-	2	2	2	2	2	7
c,	٥	o	'n	2	-	0	0	0	0	٥	٥
le le	0.5	0,5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	20
3.	0.64965	0.64965	-	-	1	÷	-	_	-	-	-
1', (aV)	-46,36495	-31,74215	-107.32728	-70,41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (eV)	7.93551	7,12083	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9,37273	9.37273
T (eV)	12,13899	6,69177	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6 90 500
٧, (٥٧)	-6,06949	-3.34589	-16.26957	-10.53337	-5.24291	-3,38732	-3.38732	-3.45250	-3.38732	-3.45250	-1 45750
F(w un) (aV)	٥	-10.36001	-15.56407	-15.56407	-14.65489	-15.56407	-15,56407	-15.35946	-15,56407	-15.35946	-15.35946
DEnism (.co no) (aV)	-0.72457	٥	0		0	0	0	0	0	0	•
1, 1, 10 ma (cV)	0.72457	-10,36001	-15.56407	-15.56407	-14.63489	-15,56407	-15.56407	-15,35946	-13.56407	-15.35946	.15.35946
E. (u, sel (cV)	-31.63537	-31,63544	-67.69451	-49,66493	-31,63533	-31,63537	-31.63537	-31.63535	-31,63537	121 62524	31329 15
12 ( atum - atam, nump . At) ( eV )	-0.72457	-0.36229	0	0	۰	-1.85836	-1.85836	-1,44915	-1.85836	-1.44915	V 164914
F. (w) (cV)	-32.35994	-31.99766	-67.69430	-49,66493	-31,63537	-33.49373	-33.49373	-33.08452	-33.49373	-33 08452	33 08452
a (10 <sup>th</sup> read /.s)	30.5436	6,45076	24.9286	24.2751	24.1759	9.43699	9,43699	15.4846	9,43699	9.55643	9.55643
E, (eV)	20.10434	4.24600	16.40846	15,97831	15.91299	6.21159	621159	10.19220	621159	6.29021	6.29021
En (eV)	-0.28705	-0.13044	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	.0 16416	717910
Figure (eP)	0.08146	0.06745 D	0.35532 (Eq. (13.458))	0.35532 (Eq. (13,458))	0.35532 (Eq. (13,458))	0.12312	0.17978	0,09944	0.12312	0.12312	0.12312
E, (cV)	-0.24632	-0.09672	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	0.10760
E (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Cylines (CV)	-32.60626	-32.09437	-67.92207	-49.80996	-31,70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
1: mar 10. 100 10 (CV)	-14,63489	-14,63489	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14,63489
L' mand (a.v.) (a.v.)	0	٥	-13,59844	-13.59844	-13,59844	0	0	0	۰	0	0
L'o leimel (CV)	5.53648	2.82459	12.49186	7.83016	3,32601	P54CE P	1 CODC P	90220 0			

Table 15.163. The total bond energies of alkyl disulfides entaulated using the functional group composition and the energies of Table 15.162 compared to the experimental values [3]. The magnetic energy 6 superine is subtracted

En land) (c)	V) values based on composition	in is given by (15.	.58).								:					P.
Formula	Name	C-S Group	S~S Group	C.M.3	. i,	H)	ر-ر (۵)	(-(. (a) C-C (b)	(c) C-C	ر-ر ر-ر	2 (a) D-D (p)	(i) )-)	E	Calculated Total Bond	Experimental Total Bond	Relative Error
Califo	Dissetty I disutfide	7	-	-	0	6	-			ľ				Energy (eV)	Energy (eV)	
S. C.	Diethyl draufade	~	-	۲۰	~	-	• ~		> <		٥ ه		0 (	34.48127	74.13	-0.00199
5	Depropy I destride	7	_	~	0	•	-				•			58,79667	58.873	
Learney.	Dist-bent diguindo	7	_	٠	۰	0		: c			۰ د	9	0	E3.11207	<b>33.169</b>	
											>		ŗ	107.99653	107510	

	- 64.6 64.6	E		(dinethyl displike)	(dimethyl disuldds)	103.2 (dinethyl disulfida)	107 (эпефолф)	112 (propane) 113.8 (butane) 110.8 (isobutane)	111.0 (butant) 111.4 (isotutane)				110,8 (Leobulane)		111.4 (isobutane) -	111.4 (fsobutane)	
	j °	ء د	109.50	109.44	111.22	103.57	10% 44	110.49	110.49	109,30	109,44	109.44	110.67	110.76	111.27	111.22	107,50
Ì	θ,	ေ															
	9	© .															
	θ,	©		70.56				K9,51	9.31		70.56	70.56					72.50
£0).	占	(eV)	c		٥	-0.72457	0			0			-1.85836	0	0	-1.85836	
– afont, msp'.	5		1.15796		970110	1,11361	1,157%			1,15796			0.81549	1.04887	1,04887	1.04887	
is Er (atom	ر.		0.75		673	-	0.75			6.73				a.73	67.0	0.75	
were used. I	ď		_		0,76(44 (Bq. 15.126))	0,64963 (Eq. (15.127))	-			~			-	,	-	-	
receding angle	Ü		-		87.0	-	-			_				81.0	25.0	0.73	
ers from the p	3	Alem 3	-		0.76144 (Eq. (15.126))	17719.0	-			-			Q.N.5499	177160	17716.0	17710.0	
), the paramet	3	Nom 1	0.16359		0.87495	0.64365 (Eq. (15.127))	0,86350			0,86359			0,81549	0,87495	0,87495	0,87495	
experimental values [1]. In the calculation of $ heta$ , the parameters from the preceding angle were used. $E_{ m t}$ is $E_{ m t}$ atom, my $^{\prime}$ AO).	Atom 2	Hybridization Designation	Ξ		5	-	Ŧ			x			a	-		-	
res [1]. In th	E	Alen 3	¥		103501-	-14,82575	×			=			-16.63412 . C.	-14.82575	-14.8353	-14,11373	
xperimental valu	Atom I	Hybridization Designation	7		s	s	,			1			22	7	-	77	
offides and e	E	į	.15 75493		-15,45033	10036.01-	-15,73493			.13.75493			-16,68412	-15,55033	-13,3503	-15.35033	
Falkyi dis	,,,,	Aires (a,)	3.4752		4,6220	5.701.7	3,425			3 4252			4,7958	4,1633	697	4.705#	
raneters of	26.	j &	203711		3,42910	3,42910	2,11106			2,09714			2,91547	2,11323	1177115	2,90327	
and sagile pa	72.	[ e	11001		209711	3 82646	2,11106			2.09711			291547	2,91547	13127	2.90327	
Table 15.164. The bond angle parameters of alkyl disulfides and	Appeas of Augila		H.JH/	# JK	ZHC, N	Zw.	Methylese ZHC H	לב"ב"ב.	н".5".Ж	Marks H	33.1/	3 1 1 1	70.70	H".J'.T	N.7.72	7,7,7	7.3.37

SULFOXIDES  $(C_n H_{2n+2}(SO)_n, n = 2,3,4,5...\infty)$ 

The alkyl sulfoxides,  $C_n H_{2n+2}(SO)_m$ , comprise a C-SO-C moiety that comprises C-S and SO functional groups. The alkyl portion of the alkyl sulfoxide may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in sulfoxides are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^22s^22p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  ${}^3P_2$ . The SO functional group comprises a double bond between the two unpaired electrons of O. The sulfur 15 atom is energy matched to the  $C2sp^3$  HO. In alkyl sulfoxides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), and the S AO has an initial energy of  $E(S) = -10.36001 \, eV$  [38]. To meet the equipotential condition of the union of the  $S = O H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the S = O-bond MO given by Eqs. (15.68) and (15.70) is

$$c_{2}(O \text{ to } S3sp^{3} \text{ to } C2sp^{3}HO) = \frac{E(O)}{E(S)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-10.36001 \text{ eV}}(0.91771)$$

$$= 1.20632$$
(15.128)

The S atom also forms a single bond with each of the  $C2sp^3$  HOs of the two C-S groups. The formation of these bonds is permitted by the hybridization of the four electrons of the S3p shell to give the orbital arrangement:

where the quantum numbers  $(\ell, m_{\ell})$  are below each electron. The 3s shell remains unchanged. Then, the Coulombic energy  $E_{Coulomb}(S, 3sp^3)$  of the outer electron of the  $S3sp^3$  shell given by Eq. (15.118) with  $r_{3sp^3} = 1.17585a_0$  (Eq. (15.119)) is  $-11.57099 \ eV$ . Using Eq. (15.16) with the radius of the sulfur atom  $r_{16} = 1.32010a_0$  given by Eq. (10.341), the energy  $E(S3sp^3)$  of the outer electron of the  $S3sp^3$  shell is given by the sum of  $E_{Coulomb}(S3sp^3)$  and E(magnetic):

$$E(S3sp^{3}) = \frac{-e^{2}}{8\pi\epsilon_{0}r_{3sp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}r_{16}^{3}}$$

$$= \frac{-e^{2}}{8\pi\epsilon_{0}1.17585a_{0}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}(1.32010a_{0})^{3}}$$

$$= -11.57099 \ eV + 0.04973$$

$$= -11.52126 \ eV$$
(15.130)

Then, the hybridization energy  $E_{hybridization}(S3sp^3)$  of the  $S3sp^3$  HO is

$$E_{hybridization}(S3sp^{3}) = E(S3sp^{3}) - E(S)$$

$$= -11.52126 \ eV - 10.36001 \ eV$$

$$= -1.16125 \ eV$$
(15.131)

The SO group is matched to the C-S group with which it shares the common 10 hybridized S atom. Consequently,  $E_{hybridizedion}(S3sp^3)$  is subtracted from  $E_T(Group)$  in the determination of  $E_D(Group)$  (Eq. 15.56)). Furthermore, the energy of the S=O-bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with the energy matched to the final energy of the hybridized S atom such that  $E(AO/HO) = E(S3sp^3) = -11.52126 \, eV$  and  $E(S3sp^3) = -11.52126 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \, eV$  and  $E(S3sp^3) = -11.6125 \,$ 

The C-S group is solved as an energy minimum by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell and by hybridizing the four S3p electrons to form a  $S3sp^3$  shell, and the sharing of electrons between the  $C2sp^3$  HO and the  $S3sp^3$  HO to form a MO permits each participating orbital to decrease in radius and energy. Using the Coulombic

energy of the  $S3sp^3$  shell,  $E_{Coulomb}(S3sp^3)$  given by Eq. (15.120) in Eq. (15.63), the  $S3sp^3$ -shell hybridization factor,  $c_2(S3sp^3)$ , is

$$c_2(S3sp^3) = \frac{E_{Coulomb}(S3sp^3)}{E(H)} = \frac{-11.57099 \ eV}{-13.60580 \ eV} = 0.85045$$
 (15.132)

As in the case of thiols, sulfides, and disulfides, the energy of sulfur is less than the 5 Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus,  $c_1$  and  $c_2$  are equal to one in Eq. (15.52), and the energy matching condition is determined by the  $C_2$  parameter. In alkyl sulfoxides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)) and the  $S3sp^3$  HO has an energy of  $E(S3sp^3) = -11.52126 \, eV$  (Eq. (15.130)). To meet the equipotential condition of the union of the C-S  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.52) for the C-S-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ S3sp^3\right) = \frac{E\left(S3sp^3\right)}{E\left(C,2sp^3\right)}c_2\left(S3sp^3\right) = \frac{-11.52126\ eV}{-14.63489\ eV}(0.85045) = 0.66951\quad(15.133)$$

As in the case of thiols, sulfides, and disulfides, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the C-S-bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with  $E(AO/HO) = 0 \qquad \text{and} \qquad E_r(AO/HO) = \Delta E_{H_2MO}(AO/HO). \qquad \text{For sulfoxides,}$   $\Delta E_{H_2MO}(AO/HO) = -0.72457 \ eV. \qquad \qquad \text{Further} \qquad \text{equivalently,}$   $E_r(atom-atom, msp^3.AO) = -0.72457 \ eV \ \text{(Eq. (14.151))}.$ 

The symbols of the functional groups of branched-chain alkyl sulfoxides are given in Table 15.165. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfoxides are given in Tables 15.166, 15.167, and 15.168, respectively. Consider that the C-S bond is along the x axis in the xy-plane. The S nucleus is at the focus +c and the C nucleus is at the focus -c. The elliptic angle θ' is taken as counterclockwise from the x-axis for S and as clockwise from the -x-axis for C. The total energy of each alkyl sulfoxide given in Table 15.169 was calculated as the sum over the integer multiple of each E<sub>D</sub>(Granp) of Table 15.168 corresponding to functional-

group composition of the molecule. The bond angle parameters of alkyl sulfoxides determined using Eqs. (15.79-15.108) are given in Table 15.170.

Table 15.165. The symbols of functional groups of alkyl sulfoxides.

Functional Group	Group Symbol
C-S	C-S
SO	SO
CH <sub>3</sub> group	$C-H\left(CH_{3}\right)$
CH <sub>2</sub> group	$C-H\left(CH_{2}\right)$
СН	C – H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

0.15329 0.55472 0.57429 0.57429 0.18708 0.18708 0.18708 0,45117

1	1							П
	(i) )—)	Стопр	2.107.2	1.45164	1.53635	1.532 (propane) 1.531 (burane)	1,52750	0.68888
	(a) 2-2	Споир	2.10725	1.45164	1.53635	1,532 (propane) 1,531 (butane)	1.52750	0.68888
	(P) ) - )	Group	2.12499	1,45744	1,54280	1.532 (propane) 1.533 (burane)	1.54616	0.68600
	(a) 2-2	Group	2,10725	1.45164	1.53635	1.532 (propane) 1.531 (butane)	1.52750	0.68888
	(C-C(b)	Group	2.12499	1,45744	1,54280	1.532 (propane) 1.531 (butane)	1.54616	0.68600
	C-C (4)	Group	2.12499	1.45744	1.54280	1.532 (propane) 1.531 (butane)	1.54616	0.68600
-	H-3	Oroup	1.67465	1.05661	1.11827	1.122 (isobutane)	1.29924	0.63095
.S. I .	(-H (CH.)	Group	1.67122	1,05553	617[1.1	1.107 (C - H propane) 1.117 (C - H butane)		. 0.63159
experimental value	(.H.) H)	Огоир	1.64920	1.04856	1,10974	1.107 (C-H propane) 1.117 (C-H butane)	1.27295	0,63580
neters of alkyl sulloxides and experimental values	os	Group	1.98517	1.408%	1.49118	1,485 (dimethyl sulfoxide)	1,39847	0,70974
able (3.100. The geometrical bond parameter	C-5	Group	1.87325	1,67271	1.77031	l. 799 (dimethyl sulfoxide)	0.84328	0.89294
1 2016 13. 150.	Parameter		u (a,)	(a) (a)	Bond Length 2c' (A)	Exp. Bond Length (A)	b,c (a,)	,

Table 15.167. The MO to HO intercept geometrical b	netrical bon	d paraneters of	bond parameters of alkyl sulfoxides. $R, R', R''$ are $R$ or alkyl groups. $E_r$ is $E_r$ and $\pi$ atom, any $\pi(Q)$ .	R, K', K" are	H or alkyl group	DS. Er is Er (0	ikon – atom, ms	p. AO).							
Bond	Atom	F,	f.	Ŀ	Ę,	Final Total	,	,	Erratura	E(C2sp')	.θ	6	6,	ď	
		(eV) Bond 1	(eV) Bond 2	(aV) Band 3	(eV) Bond 4	Chy.	(%)	(°)	(eV) Final	(c.v.) Final	©	ε	0	(%)	
R,S=0	55	0	-0.36229	-0.36229			1,32010	0.87495	-15.55033		87.67	100.22	38.00	1.56425	
R,S=0	0	0	-		٥		1,00000	0,91771	-14.12575		84.06	05.94	40.75	1.50400	
R, -50	54	-0.36220	0.34229	٥	0		1,32010	0.87495	-15.55033		129.35	50.65	53.36	1,11799	
H,C S(O) - C,H,CH,R	C,	-0,36229	a	0	٥	-451.9779%	17710.0	0.89582	-15.18804	-14,99717	130.19	18'63	54.24	1.09461	
H,C, -S(O) - C,H,CH,R	ú	-0.36229	-0.92918	0	0	-152,90716	17710,0	0,84418	-16.11722	-15.92636	128.05	51.95	52.03	1.15245	, ,
с – н (сн.)	ز	#1626'U	0	0	0	-152.54487	12416'0	0.86359	-15.75493	-15,56407	61'11.	15.501	15.15	1,23564	
C-H (CH;)	٤	0.9291R	.0,92918	0		-153,47406	17716.0	0.81549	-16.63412	-16,49323	GR 47	111.53	33.84	1.35486	
C-H (CH)	Ü	X1629.0-	#1620.0°	\$1626'O-	0	-154 40324	17716.0	0.77247	-17.61330	-17.42244	61.10	00'811	31.37	1.42988	
H.C.C.H.CH. — H.C.C.H.CH. —	ن	-0.9291#	0	O	0	-152.54487	177160	0,86359	-15.73493	-15,36407	23.53	#1'911	30,01	1.83879	
H,C,C,H,CH, (C,-C, (a))	ئ	-0.9291и	-0.92918	b	0	-[53,47406	17716.0	0,81549	-16 61412	-16.49325	19/95	65.EE.1	24,06	068067	
n - H f (, (H, C, - R') HCH; - (C - C (b))	ď	#1626'D-	810ZV,0.	#1676'D*		-154.40324	17716.0	0.77247	-17.61330	-17,4224H	48.30	02.161	21,90	1.971	
$(n-H_2C_*(R^*-H_2C_*)C_*(R^*-H_2C_*)C^*H_2-(C-C_1(0))$	ئ	-0.9291R	-0.72457	-0.72457	-0.72457	-154.71860	17160	0.75880	-17.92866	-17,7379	48.21	131.79	11.74	1,95754	1
(כ. – כ. (ק)) ונסנ"כ" (H"כ" – א.) אניא" –	ڻ	N 1026'U-	810 <u>7</u> 0.0.	8   626'0-	e	-154,40324	17710.0	0.77247	-17,61330	-17.42244	48.30	131.70	21.90	1.97162	1
$(C-C'(R-H;C_s)C_s(R^n-H;C_s)CH_s - C-C'(s))$	ڻ	-0.T24S7	-0.72457	-0.72457	-0.72457	-154.51399	17716.0	0.76765	-17.92866	CT.ET.T.	30.04	129.96	22.66	1.94462	١
(כ – כ (נ) ופונג"כ" (H²C, – נו.) אכאי –	υ*	-0.72457	81626.0-	-0.9291 x	·0	-134.19163	17710.0	0,78155	-17.40869	-17,21785	52.78	12723	24,04	1,92443	1
hoC,(R'-H,C,)C,(R'-H,C,)CH,-	ť	-0.72457	-0.72457	-0,72457	-0.72457	-154.51399	17710.0	6,767.6	.17.92866	יחנו,ו.	50.04	129.96	27.66	1,94462	ı

Parameters	C-S Granb	Group	χ. Έ	Grans	Group	Group Group	Group	Group	Group Group	Group	Group Group
n,	-	2	2	2	-	-	-	_	-	-	-
n,	0	0	2	-	0	0	0	0	0	0	0
n'	0	0	0	0	0	0	٥	0	0	0	0
	0.5	0.5	0.75	0.75	0.75	0.5	5.0	5.0	0.5	6.5	0.5
	0.66951	-	-	-	-	-	-	_	-	-	-
	-	_	-	_	-	_	_	-	1	-	-
	-	1.20632	0.91771	0.91771	0.91771	0.91771	0.91771	17716,0	17719,0	17716.0	17716.0
6.	٥		0	-		0	a	0	_	1	0
	2	•	-	-	-	7	7	2	2	2	2
5	0	-		2.	-	0	0	0	0	0	0
	0.5	0.5	0.75	0.75	0.75	0.5	0.5	6,0	0.5	0.5	0.5
,,,	0.66951	1	-	-	-	-	_	-	-	1	1
V, (eV)	46.73032	-82.63003	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (aV)	8.13401	19,31325	38.92728	25.78002	12.87680	9,33352	9.33352	9.37273	9.33352	9,37275	57272.9
T (aV)	12.47306	20.81183	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
7 (07)	-6.23653	-10.40592	-16.26957	-10,53337	-5.24291	-3.38732	-3.38752	-3.45250	-3.38732	-3.45250	-3.45250
E(.v. an) (eV)	0	-11.52126	-15,56407	-15,56407	-14.63489	-15,56407	-15,56407	-15,35946	-15.56407	-15,35946	-15.35946
ΔΕ, 10 (m m) (cV)	-0.72457	-1.16125	0	0	0	0	0	0	0	0	0
15. (no no) (aV)	0.72457	-10,36001	-13.56407	-15,56407	-14.63489	-15.56407	-15,56407	-15,35946	-15,56407	-15,35946	-15.35946
( rand (cV)	-31.63521	-63.27088	-67.69451	-49,66493	-31.63533	-31.63537	-31.63537	-31,63535	-31,63537	-31.63535	-31.63535
Er (atum - atam, nxp2, AO) (eV)	-0.72457	0	0	0	0	-1.85836	-1.85836	-1,44915	-1.85836	-1.44915	-1.44915
Er (100) (cV)	-32,35994	-63.27074	-67.69450	-49,66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
@ (10" rod /s)	30,8880	17,6762	24.9286	24.2751	24.1759	6954.6	9.43699	15.4846	9.43699	9.55643	9.53643
Er (eV)	20.33104	11,63476	16,40846	15.97831	15.91299	631159	621159	10.19220	6.21159	6.29021	120679
E. (eV)	-0.28866	-0.21348	-0.25352	-0.25017	-0.24966	\$1691.0-	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Erm (cV)	0.08543	0.12832	0.35532 (Eq. (13.458))	0,35532 (Eq. (13,458))	0,35532 (Eq. (13,458))	0.12312 f21	0.17978	0.09944	0.12312	0.12312	21221.0 [5]
En (eV)	-0.24595	-0.14932	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
(cV)	0.14803	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
External (cV)	-32.60589	-63.56937	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33,24376	-33.59732	-33,18712	-33.18712
E may (c. 10 110) (cV)	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489
Emen le, en in) (eV)	0	-1.16125	-13.59844	-13,59844	-13.59844	0	0	0	0	0	0
( to 1 ( N)	133611	3.86856	12.49186	7.83016	3,32601	4.32754	4.29921	3.97398	4.17951	3.62128	75216 E

Table (5.169. The total band energies of alkyl suffixides calculated using the functional group composition and the energies of Table 15.168 campared to the experimental values [3].

Formula Name C-C (a) C-C (b) C-C (c) C-C (d) C-C (e) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-C (f) C-

	Exp. 6	E	Offerenty cutters	(danethył sulfavi	(propere)	112 (propers) 113,8 (butane) 110,9 (itobutane)	(111.0 (botane) (11.4 (sobutane)	1103 (dincin'i sullex			110,8 (Isobutane)		111.4 (Stobatane)	111.4 (isobutane)	
	Cal. 0		96.20	106.48	# #	110.49	110.49	10).50	100.44	109.44	110,67	110.76	11.27	111.27	
	6.	<u> </u>	L						L						
	6-	Ξ_	L												
	6.	<u> </u>	L			1269	15.69		35	20.56		_			1
osp'.AO).	£,	<u> </u>	-1,15136	-1,653,76	0			¢			1,85836	p	Đ	-1.163836	
m – atom, n	<del>ر</del> د		0,82562	0.87489	1.15796			1.15796			0,11549	LOARRY	1,048X7	f,04887	
Fris Er a	را		-	-	6.75			0.75			-	6.75	57.0	27.0	
ere used.	Ç		-	-	J			-			-	-	~	-	
ling engle w	5		-	-	-			1			1	0.75	0.75	0,75	
rom the preced	5	i	0,12552	0.8335 (Eq. (15.114))	-			1			อะรเมช	177.18.0	(17719.0	n.91771	
parameters f	<b>3</b> ]		0.K75G2	0.89312	0.86359			0.36359			0,81549	0,\$7495	0,87495	0,87495	
iculation of $\theta_r$ , the	Atom 2 Hybridication	Designation (Table 15.3.A)	12	0	Ξ			Ŧ			15		,		
I). In the ca	E		1562771-	יואניינו. ט	¥			Ξ			-16,08412 (*	-14,172575 C	.14.R2575	-14,82575 C	
enimental values (	Atom   Hybridizaton	Designation (Table 15.3.A)	17	7	,			7			ы	ş	\$	3	
ides and exp	Grand		15647911	-15.1×104 C.	-15.75493			-15.75493			-16.6BH12	-15.55033	13,33033	-15.55033 C' <sub>k</sub>	
alkyl sulfox	Zc. Tominal	Atoms ( 17 <sub>6</sub> )	4.9800	4.9508	3,4252			3,4352			4.738K	4.1633	4.1633	4.705#	_
rameters of	7¢.	(°)	334541	2,81792	2,11104			2,09711			291547	2,(1323	2,09711	7,503,27	
and angle pa	įĸ	(°)	3,3454!	3,34541	211106			2.09711			2,91547	2.91347	2.91547	2.90327	
Table 13,170. The bord angle parameters of alkyl suifoxides and experimental values [1]. In the calculation of $\theta_o$ , the parameters from the proceeding angle were used. E, is E, (atom - otom, map. AO)	Alone of Acade		*.x*.	CC*30	Methodowe ZHC, H	אנ"נ"נ".	H'S'S	H"JH7	``,``,``,`` <b>X</b> (.`C,'\.'	H'J',J7	۱۹۵ ز. حرد در در د	7) *** 7'', '', 'H	LC,C,H	מנות" כת"נ"נ"	7

SULFOXIDES 
$$(C_n H_{2n+2}(SO)_n, n=2,3,4,5...\infty)$$

The alkyl sulfoxides,  $C_n H_{2n+2}(SO)_m$ , comprise a C-SO-C moiety that comprises C-S and SO functional groups. The alkyl portion of the alkyl sulfoxide may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in sulfoxides are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^22s^22p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  ${}^3P_2$ . The SO functional group comprises a double bond between the two unpaired electrons of O. The sulfur 15 atom is energy matched to the  $C2sp^3$  HO. In alkyl sulfoxides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), and the S AO has an initial energy of  $E(S) = -10.36001 \, eV$  [38]. To meet the equipotential condition of the union of the  $S = O H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the S = O-bond MO given by Eqs. (15.68) and (15.70) is

$$c_{2}(0 \text{ to } S3sp^{3} \text{ to } C2sp^{3}HO) = \frac{E(O)}{E(S)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-10.36001 \text{ eV}}(0.91771)$$

$$= 1.20632$$
(15.128)

The S atom also forms a single bond with each of the  $C2sp^3$  HOs of the two C-S groups. The formation of these bonds is permitted by the hybridization of the four electrons of the S3p shell to give the orbital arrangement:

25 
$$\frac{3sp^{3} \text{ state}}{\uparrow} \qquad \uparrow \qquad \uparrow \qquad \uparrow \\ 0,0 \qquad 1,-1 \qquad 1,0 \qquad 1,1$$
 (15.129)

where the quantum numbers  $(\ell, m_{\ell})$  are below each electron. The 3s shell remains unchanged. Then, the Coulombic energy  $E_{Coulomb}(S, 3sp^3)$  of the outer electron of the  $S3sp^3$  shell given by Eq. (15.118) with  $r_{3sp^3} = 1.17585a_0$  (Eq. (15.119)) is  $-11.57099 \ eV$ . Using Eq. (15.16) with the radius of the sulfur atom  $r_{16} = 1.32010a_0$  given by Eq. (10.341), the energy  $E(S3sp^3)$  of the outer electron of the  $S3sp^3$  shell is given by the sum of  $E_{Coulomb}(S3sp^3)$  and E(magnetic):

$$E(S3sp^{3}) = \frac{-e^{2}}{8\pi\varepsilon_{0}r_{3sp^{3}}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}r_{16}^{3}}$$

$$= \frac{-e^{2}}{8\pi\varepsilon_{0}1.17585a_{0}} + \frac{2\pi\mu_{0}e^{2}\hbar^{2}}{m_{e}^{2}\left(1.32010a_{0}\right)^{3}}$$

$$= -11.57099 \ eV + 0.04973$$

$$= -11.52126 \ eV$$
(15.130)

Then, the hybridization energy  $E_{hybridization}(S3sp^3)$  of the  $S3sp^3$  HO is

$$E_{hybridization}(S3sp^{3}) = E(S3sp^{3}) - E(S)$$

$$= -11.52126 \ eV - 10.36001 \ eV$$

$$= -1.16125 \ eV$$
(15.131)

The SO group is matched to the C-S group with which it shares the common 10 hybridized S atom. Consequently,  $E_{hybridization}\left(S3sp^3\right)$  is subtracted from  $E_T\left(Group\right)$  in the determination of  $E_D\left(Group\right)$  (Eq. 15.56)). Furthermore, the energy of the S=O-bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with the energy matched to the final energy of the hybridized S atom such that  $E\left(AO/HO\right) = E\left(S3sp^3\right) = -11.52126 \, eV$  and a node of  $E_T\left(AO/HO\right) = E\left(S\right) = -10.36001 \, eV$ . Also,  $E_T\left(atom-atom,msp^3.AO\right)$  of the S=O bond is zero since there are no bonds with a  $C2sp^3$  HO.

The C-S group is solved as an energy minimum by hybridizing the 2s and 2p AOs of the C atom to form a single  $2sp^3$  shell and by hybridizing the four S3p electrons to form a 20  $S3sp^3$  shell, and the sharing of electrons between the  $C2sp^3$  HO and the  $S3sp^3$  HO to form a MO permits each participating orbital to decrease in radius and energy. Using the Coulombic

energy of the  $S3sp^3$  shell,  $E_{Coulomb}(S3sp^3)$  given by Eq. (15.120) in Eq. (15.63), the  $S3sp^3$ -shell hybridization factor,  $c_2(S3sp^3)$ , is

$$c_2(S3sp^3) = \frac{E_{Coulomb}(S3sp^3)}{E(H)} = \frac{-11.57099 \ eV}{-13.60580 \ eV} = 0.85045$$
 (15.132)

As in the case of thiols, sulfides, and disulfides, the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus,  $c_1$  and  $c_2$  are equal to one in Eq. (15.52), and the energy matching condition is determined by the  $C_2$  parameter. In alkyl sulfoxides, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)) and the  $S3sp^3$  HO has an energy of  $E(S3sp^3) = -11.52126 \, eV$  (Eq. (15.130)). To meet the equipotential condition of the union of the C-S  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $C_2$  of Eq. (15.52) for the C-S-bond MO given by Eqs. (15.68) and (15.70) is

$$C_2\left(C2sp^3HO\ to\ S3sp^3\right) = \frac{E\left(S3sp^3\right)}{E\left(C,2sp^3\right)}c_2\left(S3sp^3\right) = \frac{-11.52126\ eV}{-14.63489\ eV}\left(0.85045\right) = 0.66951\ \ (15.133)$$

As in the case of thiols, sulfides, and disulfides, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the C-S-bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in Eq. (15.42) with  $E(AO/HO) = 0 \qquad \text{and} \qquad E_T(AO/HO) = \Delta E_{H_1MO}(AO/HO). \qquad \text{For sulfoxides,}$   $\Delta E_{H_2MO}(AO/HO) = -0.72457 \, eV. \qquad \qquad \text{Further} \qquad \text{equivalently,}$   $E_T(atom-atom, msp^3.AO) = -0.72457 \, eV \quad \text{(Eq. (14.151))}.$ 

The symbols of the functional groups of branched-chain alkyl sulfoxides are given in Table 15.165. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfoxides are given in Tables 15.166, 15.167, and 15.168, respectively. Consider that the C-S bond is along the x axis in the xy-plane. The S nucleus is at the focus +c and the C nucleus is at the focus -c. The elliptic angle θ' is taken as counterclockwise from the x-axis for S and as clockwise from the -x-axis for C. The total energy of each alkyl sulfoxide given in Table 15.169 was calculated as the sum over the integer multiple of each E<sub>D</sub> (comp) of Table 15.168 corresponding to functional-

group composition of the molecule. The bond angle parameters of alkyl sulfoxides determined using Eqs. (15.79-15.108) are given in Table 15.170.

Table 15.165. The symbols of functional groups of alkyl sulfoxides.

Functional Group	Group Symbol
C-S	C-S
SO	SO
CH₃ group	$C-H$ $(CH_3)$
CH₂ group	$C-H$ $(CH_2)$
СН	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C) + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 +	C-C (e)
CC (t to iso-C)	C-C (f)

Parameter	S : 2	g ျှ	C-H (CH,)	('H') H - J	H-3	C-C(8)	C-C(b)	(5)	0-0-0	0-0	0,0
1	dono	dnano	Oroup	Group	Group	Group	Group .	Group	Group	Group	Group
0 (0,	1.87525	1.98517	1.64920	1.67122	1.67465	2.12499	2,12499	2.10725	2 12/00	2 10276	
د. (۵)	1.67271	1,40896	1.04856	1.05553	1,05661	1 45744	1 45744	1 46161		1.10/23	2.107.2
Bond							44/C#1	40104	1,45744	1,45164	1,45164
Zc' (A)	1.77031	. 1.49118	1.10974	1,11713	1.11827	1.54280	1.54280	1.53635	1.54280	1.53635	1,53635
			1107								
Length	1.799	1.485	H-2)	# - U)		1.532	1.532	1.532	1.532	1.532	1.532
·T	(dimethyl sulfoxide)	(dimethyl sulfoxide)	propane)	propane)	(isobutane)	(propane)	(propune) 1,531	(propans)	(propane)	(propane)	(propane)
-			(C-H butane)	(C-H butane)		(butane)	(butane)	(butane)	(butanc)	(butane)	(Amelian)
h,c (a,)	0.84328	1.39847	1.27295	1,29569	1,29924	1.54616	1 54616	1 53260	7.075		
	0.89294	70000	003290	22.60	, , , ,		21200	00136.1	010401	1.52750	1.52750
		20000	00000		2002						

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	ometrical by	and parameters o	falkyl sulfoxide.	S. R.R.R. are	H or alkyl group	3s. E, is E, (a	tiom - atom, as	(07,0							
Bond	Atom	3									į				
		(e, 7, Bond 1	(eV)	(cV)	(eV)	Energy	(e) [	`§ @	15	E(C2sp²)	.e)	6.€	8,	d, 0	j. (
					- Dung	3 3	:	;	Final	Fina	:	>	>	(a)	(°)
A,5 = C	×	٥	-0.36229	-0.36229	c		1,32010	0.87495	14 65032						
אים מיי	0	0	c		٥		00000				19.78	1200	38,00	1.56425	0.15529
R, 50	>.	0,36229	-0.36229				1.0000	12160	-14,82575		84.DG	95,04	40,75	1,50400	0.00504
H,C, -S(O) - C, H, CH, R	ن	-0.36229	0		, .	002200	1,32010	0.87495	.15.55033		120,35	50.65	53.36	1.11799	0.55472
H,CS(O) - C,H,CH,R	ن	-0.36229	.0 92918		, ,	10170761-	1//160	O.ROSR2	-15.18804	-14.99717	130.19	49.81	34.24	1.09461	0.57809
C-H (CH,)	١	A 93117k				-134,90/16	12/16.0	0,84418	-16.1172	-13.92636	128.05	\$1.95	52.03	1.15245	0.52026
C-H (CH.)	. ;		-		•	-152.54487	0.91771	0.8G359	-15.75493	-15.56407	77.49	102.31	41.48	1,23564	0.18708
(c)		-0.92918	-0.9291R		0	-153.47406	12160	0.81549	11719791-	-14.49325	68.47	11.53	33.84	135,000	0 30000
( -H (tH)	ان	-0.9291K	-0.9291X	-0.92918	•	-154,40324	17716.0	0,77247	-17,61330	-17.42244	91.19	00 411	1	2000	erico.u
7,5,5,4,5,4,5,4,5,4,5,4,5,4,5,4,5,4,5,4,	ن.	-0.9291#	0	0		-152.5487	17710.0	0.86359	-15.75493	-15 \$6407	6		76.16	L. & CONS	0.37226
H,C,C,H,CH, -	,												24,08	1.83879	0.38106
(C-C (a))	;	8   676 in-	-0.929FK	0	0	-153,47406	12216'0	0.81549	-16.68412	-16.49325	\$6.41	123.59	24.06	1,90890	0.43117
$(C-C, \{b\})$	ن	-0.92918	-0.9291R	#1620.0-	•	-154,40324	Q.91771	0,77247	-17,61330	-17,42244	62.30	8 5	8 7		
11-H3C,(14-H3C,)C,(14-H2C,)CH,-	,												JE:13	1.97102	0.51388
(C-C (e))	,	.0.92918	-0,72657	-0.72457	-0.72457	154.7(860	0.91771	0.73119	-17.92866	-17.7379	48,21	67,161	21.74	K126.1	0.50370
$(C = C, \{d\})$	ئ	N1626'0-	442918	.0.92918	0	-154.40324	0,9171	0,77247	-17,61330	-17,42244	02.47	5	1		
$lenC_{*}(R'-H_{*}C_{*})C_{*}(R'-H_{*}C_{*})CH_{*}-$ (C - ( (0))	ۍ	-0,72457	-0.72457	-0.72457	-0.72457	.134.51300	17716.0	0.76763	- 17 078CA	1			DC17	2016	0.51388
$mHC_{s}C_{s}(H_{2}C_{s}-R^{s})HCH_{3}-$	;										80'00	96/67	22.06	1,9462	0.49298
(C-C(f))	3	10,1,000	-0.92911	-0.92918	4	-154.19863	17716.0	0.78135	-17.408/60	-17.21783	52.78	17771	2.02	1,92443	0.47279
(C-C(0))	ئ	41.72457	-0.72457	-0.72457	40.72457	-154.31399	14416.0	0.76763	-17.92866	0.7.57.71	20.05	120.96	2,00	5880	1000
									_	_	_				

	C-S Group	SO Group	r.H., Groun	C'H.	Graup	Group	(e) (J-() (g) (d) (d) (d) (d) (d) (d) (d) (d) (d) (d	C-C (c) Group	C-C (d) Group	Group Group	Group
п,	-	2		2	-	-	-	1	1	1	
u,	٥	0	7	-	0	0	0	0	0	0	0
u'	0	0	0	0	0	0	0	0	0	0	0
	0.5	0.5	0.75	0.75	0.75	6.5	6.0	6.0	0.5	0.5	0.5
	0.66951	-	-	-	-	-	1	-	-	1	-
	-	-	_	-	_	_	-	-	1	-	. 1
	-	1.20632	17710	17716.0	0.91771	0.91771	17716.0	0.91771	0.91771	17716.0	17719.0
6,	0	0	0	-	-	0	0 .	٥	-	-	O
ر.	2	Þ	1	1	1	2	7	2	2	2	2
ر	0	-	3	7	-	0	0	0	0	0	0
	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	2.0	0.5	0.5
. *	0.66951	-	-	-	-	_	-	-	-		-
1', (cl')	-46.73032	-82,63003	-107,32728	-70,41425	\$1021.28-	-28.79214	-28.79214	-29,10112	-28.79214	-29.10112	-29,10112
V, (eV)	8.13401	19,31325	38.92728	25.78002	12.87680	9,33352	9.3352	9,37273	9,33352	9.37275	9,57273
T (dV)	12.47306	20.81183	32,53914	21.06675	10.48582	6,77464	6.77464	6.90500	6.77464	6,90500	6.90500
V, (eV)	-6.23653	-10.40592	-16.26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E (.v 110) (cV)	0	-11.52126	-15.56407	-15.56407	-14.63489	-15.56407	-15,56407	-15.35946	-15.56407	-15.35946	-15.35946
DE ILLIAN (SO MO) (CV)	-0.72457	-1.16125	0	0	0	0	٥	0	0	0	0
F. (w m) (cV)	0.72457	-10.36001	-15,56407	-15.56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15,35946
Fr (u,sa) (cV)	-31.63521	-63.27088	-67.69451	-49.66493	-31,63533	-31.63537	-31.63537	-31.63535	-31,63537	\$2529'12-	-31,63535
F. (atum - atom, msp. An) (eV)	-0.72457	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1,44915
E, (se) (eV)	-32,35994	-63.27074	-67,69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33,08452	-33.08452
(x/pa, 101) a	30.8880	17.6762	24.9286	24.2751	24.1759 .	9,43699	9.43699	15.4846	9.43699	9.55643	9.55643
$E_{\kappa}$ (eV)	20.33104	11.63476	16,40846	15.97831	13.91299	6,21159	6.21159	10.19220	621159	12062.9	120679
E, (eV)	-0.28866	-0.21348	-0.25352	-0.25017	-0.24966	-0.16315	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Erm (cV)	0.08543	0.12832	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0,35532 (Eq. (13,458))	0.12312	0.17978	0.09944	0,12312 (2)	0.12312	0.12312
E (cV)	-0.24595	-0.14932	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E (cV)	0,14803	0.11441	0.14803	0.14803	0.14805	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803
Er (may) (cV)	-32,60589	-63.56937	-67.92207	-49.80996	76707,1E-	-33.59732	-33,49373	-33.24376	-33.59732	-33.18712	-33.18712
E le, so m) (eV)	-14.63489	-14,63489	-14,63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489
E 16, 10 00) (eV)	0	-1.16125	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
/: (mm) (cV)	1 33611	3.86856	12.49186	7.83016	1 27601	134C2 1	4 7007 1	1 07008	13041 7	26167.5	401974

Table 15.169. The total bond energies of alkyl sufficients using the functional group composition and the energies of Table 15.168 compared to the experimental values [3].

Formula Name C-C (a) C-C (b) C-C (c) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C (d) C-C S24.25 S24.25 S24.25

								_						_
	Εφ. <i>θ</i>	96.6 (dimethyl ruffocide)	106.7 (dimedirf sulfacide)	(conedoud)	112 (prepans) 113.8 (butanc) 110.8 (isobutanc)	111.0 (botane) 111.4 (isobutane)	1 (Q.3 (dimethyl sulfaxide)			110.8 (isobutano)		111.4 (isobutant)	111.4 (irobutane)	
	Cat. 0	96.20	106.89	101	110.49	110,49	05-601	109,44	109.44	19011	110.76	11127	111.27	107.50
	(C)													Γ
	e, ©													
	ø, 🖭				15.00	1509		30%	70.56					22.50
sp'.40).	(eV)	-1.85836	-1.65376	o '			0			-1,85836	o	o	-1,85836	
na caform, or	v	0.82562	0.87489	1.15796			1,137%			0.11549	1,04887	1,04887	1,04887	
5, is E <sub>7</sub> (ak	٠. ت	. 1	-	0.75			0.75			_	0.75	27.0	0,75	
rere used. 6	۲,	-	-	-			-			1	-	-	-	
fing angle w	r,	1	-	-			-			,	0.75	£7.5	6.75	
om the preced	C. Airon 3	0.82562	0.83395 (Eq. (15.114))				-			OFFIRO	1/2/16/0	17710.0	17716.0	
parametors fr	C <sub>3</sub> Alem I	0.R2562	0.89582	0.86359			0,86359			0,41549	0,87495	0.87495	0,87495	
lculation of $\theta$ , the	Atom 7 Hybridization Designation (Table (5.3.A)	Ħ	0	¥			н			25	•	-	-	
1]. In the ca	Elwinde Alm 7	-16,47951	ייסאואנוי.	н			×			(,°	-14,82575 C,	-14,x2575 (°,	-14.x2575 C,	
crimental values	Atom I  Hybridization Designation (Table 15.3.A)	17	2	,			,			27	\$	•		
ides and exp	Erants Alms 1	-16.47951	-15.1804 C,	15.73493			15,75493			-16 GR412	-15.55033	-15.35033	-15.53033 C.	
alkyl sulfox	2c' Terrind Alon (0,)	4.9%00	#6\$6°#	1,423			3,4252			4.705%	£5y1.4	4,1633	4.7958	_
rameters of	2c' Brad 2 (A,)	3,34541	2,81702	9011172			112607			2.91547	211333	114007	2,91327	
nd angle par	2¢' Rund 1 ( a <sub>a</sub> )	3,34541	3,34541	2.11106			2.09711			2,01547	215167	2.91547	7,500.2	
Table [5,170. The bond angle parameters of alkyl sulfoxides and experimental values [1]. In the calculation of \theta, the parameters from the proceding angle were used. E, is E_{\left(ann)} = atom, asp' -A(O).	A terms of Apparle	". XC.)?	08'37	Hanytone ZHC, H	*.7".77	H*:5°57	A.THC.H	'.'.'.'.''.	H"5,37	יף כ' ענ'נ'נ'	به ر" ۲۲:۲ <i>۲ "H</i>	L', ', 'H H', ', ')7	جعد درم حزد پاور "ورم"	7.7.7.

## DIMETHYL SULFOXIDE DIHEDRAL ANGLE

The dihedral angle  $\theta_{ZS=O/CSC}$  between the plane defined by the CSC MO comprising a linear combination of two S-C-bond MOs and a line defined by the S=O-bond MO where S is the central atom is calculated using the results given in Table 15.170 and Eqs. (15.105-15.108). The distance  $d_1$  along the bisector of  $\theta_{ZCSC}$  from S to the internuclear-distance line between C and C,  $2c'_{C-C}$ , is given by

$$d_1 = 2c'_{s-c}\cos\frac{\theta_{\angle CSC}}{2} = 4.9800a_0\cos\frac{96.20^\circ}{2} = 2.23423a_0$$
 (15.134)

where  $2c'_{s-c}$  is the internuclear distance between S and C. The atoms C, C, and O define 10 the base of a pyramid. Then, the pyramidal angle  $\theta_{zcoc}$  can be solved from the internuclear distances between C and C,  $2c'_{c-c}$ , and between C and O,  $2c'_{c-o}$ , using the law of cosines (Eq. (15.106)):

$$\theta_{ZCCC} = \cos^{-1}\left(\frac{\left(2c'_{C-O}\right)^2 + \left(2c'_{C-O}\right)^2 - \left(2c'_{C-O}\right)^2}{2\left(2c'_{C-O}\right)\left(2c'_{C-O}\right)}\right)$$

$$= \cos^{-1}\left(\frac{\left(4.95984\right)^2 + \left(4.95984\right)^2 - \left(4.9800\right)^2}{2\left(4.95984\right)\left(4.95984\right)}\right)$$

$$= 60.27^{\circ}$$
(15.135)

Then, the distance  $d_2$  along the bisector of  $\theta_{ZCOC}$  from O to the internuclear-distance line  $2c_{C-C}^{\dagger}$ , is given by

$$d_2 = 2c'_{c-\alpha}\cos\frac{\theta_{ZCOC}}{2} = 4.95984a_0\cos\frac{60.27^{\circ}}{2} = 4.28952a_0$$
 (15.136)

The lengths  $d_1$ ,  $d_2$ , and  $2c'_{S=O}$  define a triangle wherein the angle between  $d_1$  and the internuclear distance between O and S,  $2c'_{S=O}$ , is the dihedral angle  $\theta_{ZS=O(CS)}$  that can be solved using the law of cosines (Eq. (15.108)):

$$\theta_{ZS=O/CR} = \cos^{-1} \left( \frac{d_1^2 + (2c'_{S=O})^2 - d_2^2}{2d_1(2c'_{S=O})} \right)$$

$$= \cos^{-1} \left( \frac{(2.23423)^2 + (2.81792)^2 - (4.28952)^2}{2(2.23423)(2.81792)} \right)$$

$$= 115.74^{\circ}$$
(15.137)

(15.138)

The experimental [1] dihedral angle  $\theta_{\rm ZS=O/CSC}$  is

$$\theta_{\angle S=O/CSC} = 115.5^{\circ}$$

SULFITES  $(C_n H_{2n+2}(SO_3)_m, n=2,3,4,5...\infty)$ 

The alkyl sulfites,  $C_nH_{2n+2}(SO_3)_m$ , comprise a C-O-SO-O-C moiety that comprises two types C-O functional groups, one for methyl and one for alkyl, and O-S and SO functional groups. The alkyl portion of the alkyl sulfite may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in sulfites are equivalent to those in branched-chain alkanes.

The SO functional group is equivalent to that of sulfoxides with  $E_T(atom-atom,msp^3.AO)=0$  as given in the Sulfoxides section. The methyl and alkyl C-O 15 functional groups having  $E_T(atom-atom,msp^3.AO)=-1.44915 eV$  and  $E_T(atom-atom,msp^3.AO)=-1.65376 eV$ , respectively, are equivalent to the corresponding ether groups given in the Ethers section except for the energy terms corresponding to oscillation of the bond in the transition state.

The electron configuration of oxygen is  $1s^2 2s^2 2p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  ${}^3P_2$ . The SO functional group comprises a double bond between the S atom and the two unpaired electrons of O. The S atom also forms single bonds with two additional oxygen atoms that are each further bound to methyl or alkyl groups. The first bond-order bonding in the O-S groups is between the sulfur atom and a O2p AO of each oxygen of the two bonds. The formation of these four bonds with the sulfur atom is permitted by the hybridization of the four electrons of the S3p shell to give the orbital arrangement given by Eq. (15.129). Then, the Coulombic energy  $E_{Coulomb}(S, 3sp^3)$  of the outer electron of the S3sp³ shell given by Eq. (15.120) with  $r_{3sp^3} = 1.17585a_0$  (Eq. (15.119)) is  $-11.57099 \, eV$ . Using Eq. (15.16) with the radius of the

sulfur atom  $r_{16} = 1.32010a_0$  given by Eq. (10.341), the energy  $E(S3sp^3)$  of the outer electron of the  $S3sp^3$  shell given by the sum of  $E_{Coulomb}(S3sp^3)$  and E(magnetic) is  $E(S3sp^3) = -11.52126 \ eV$  (Eq. (15.130)).

Thus, the O-S group is solved as an energy minimum by hybridizing the four S3p 5 electrons to form a  $S3sp^3$  shell, and the sharing of electrons between the O2p AO and the  $S3sp^3$  HO to form a MO permits each participating orbital to decrease in radius and energy. As in the case of thiols, sulfides, disulfides, and sulfoxides, the energy of sulfur is less than the Coulombic energy between the electron and proton of H given by Eq. (1.243). Thus,  $c_1$  and  $c_2$  are equal to one in Eq. (15.52), and the energy matching condition is determined by the  $C_2$  10 parameter. Each  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), and the S HO has an energy of  $E(S3sp^3) = -11.52126 \, eV$ . To meet the equipotential condition of the union of the O-S  $H_2$ -type-ellipsoidal-MO with these orbitals with the oxygen that further bonds to a  $C2sp^3$  HO, the hybridization factor  $C_2$  of Eq. (15.52) for the O-S-bond MO given by Eqs. 15 (15.68) and (15.70) is

$$C_{2}(S3sp^{3} \text{ to } O \text{ to } C2sp^{3}HO) = \frac{E(S,3sp^{3})}{E(O,2p)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-11.52126 \text{ eV}}{-13.61806 \text{ eV}}(0.91771)$$

$$= 0.77641$$
(15.139)

As in the case of thiols, sulfides, disulfides, and sulfoxides, with the energy of S matched to the Coulombic energy between the electron and proton of H, the energy of the O-S-bond MO is the sum of the component energies of the  $H_2$ -type ellipsoidal MO given in 20 Eq. (15.42) with E(AO/HO) = 0 and  $E_T(AO/HO) = \Delta E_{H_2MO}(AO/HO)$ . For sulfites,  $\Delta E_{H_2MO}(AO/HO) = -0.92918 \, eV$  and equivalently,  $E_T(atom-atom,msp^3.AO) = -0.92918 \, eV$  (Eq. (14.513)) due to the maximum energy match with the oxygen AO as in the case with carboxylic acid esters.

The symbols of the functional groups of branched-chain alkyl sulfites are given in Table 15.177. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfites are given in Tables 15.178, 15.179, and 15.180, respectively. The total energy of each alkyl sulfite given in Table 15.175 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.180 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfites determined using Eqs. (15.79-15.108) are given in Table 15.182.

Table 15.177. The symbols of functional groups of alkyl sulfites.

Table 15.177. The symbols of functional gro	sups of alkyl suffices.
Functional Group	Group Symbol
C-O (methyl)	C-O (i)
C-O (alkyl)	C-O (ii)
O-SO <sub>2</sub>	O-S
SO	SO
CH₃ group	$C-H\left(CH_{3}\right)$
CH₂ group	$C-H$ $(CH_2)$
СН	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

		_					_	_		_			
	() <u>J-</u> J	dans	2 10705	2,101.2	1.45164	1.53635		1.532	(propane)	lec.	(onime)	1.52750	
	(9) 2 - 2	dinai	2 10725		1.45164	1,53635		1.532	(propane)	ice d	(normalie)	1.52750	
	C-C (d)		2.12499		1,43/44	1.54280		1.532	(propane)	(Juliane)	(comme)	1.54616	00000
	(e) U-U	-	2,10725	1.46164	1.1.2104	1.53635		1.532	(propane)	Chuffens	,	06/261	000000
	. C-C (b)		2.12499	1 45744		. 1.54280		1.532	(propane)	(butane)		01050	009890
	C-C		2.12499	1 45744		1.54280		1.532	(propare)	(butane)	1 64614	124010	0.68600
ł	dnou Guonb	1	1.67465	1.05661		1.11827			(isobutane)		1 2007		0.63095
	C-H (CH <sub>2</sub> )		1.0/122	1.05553		1.11713		L.IO7	1.117	(C-H butane)	1 79569		0.63159
1,11	C-H (CH,) Group 1.64920		1.04920	. 1.04856		1.10974		(C - H gropane)	1,117	(C-H butane)	1.27295	200000	0.63580
5	3	1 00017	1.705.1	1,408%		1,49118			(amethy) sulfoxide)		1,39847	ATOOF O	0,70974
2	3	1 70700		1,48102		1,36744		1.574	(H <sub>3</sub> ,SO <sub>4</sub> )		0.84059	0.8666	0.00
(I) 0-3	Group	1.70473		1.33968		1.41785					1.19429	0 74645	2.2.2.2
_	Group	1.80717		1.34431		1.42276					1.20776	0.74388	
Parameter		a (a,		c. (a')	Dond	Length 2c' (A)	Exp.	Bond	3		h.c (a,)	ŭ	

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	Atom	E	ų	E	4	Final Total	1	F	1	$E(C2sp^2)$	60	<b>o</b> - :	6	0	<b>6</b> "
	٠.	રે ક	 (S)	(eV)	(eV)		<u>e</u>	(°)	S in	§,	©	<u> </u>	©	ું ક	(°
:		n niibo	Pound 2		200	5				ring					
(RO), S = O.	s	0	-0.46459 :	-0.46439	. 0		1,52010	0.86339	-13,75493		71.56	101.44	37.23	1,58026	0.17130
(RO); S = 0	0	0	-	•	-		1.0000	17710.0	-14,82575		14.06	95.54	40.75	1.50400	0.09304
CH.O S(0)OR'	· .	0.46439	-0.46459		0		1,32010	0.86339	-15.75493		126.68	23.22	55.47	12576'0	0.51581
CH,O, - S(O)OR' (C - O (1))	0,	-0.46459	. 471457 .	0	0		000001	0.84957	-16,01492		126.03	53.97	34.81	0,08(33	0.49969
RCH,0, - S(O)OR"	c.	-0.46459	-0.82(SH -	. 0	. 0		1.00000	0.34418	-16.11722		125.77	54,23	54.56	0.98753	0.49349
H,C, -0,5(0)0R	0	0.72457	-0.46459 .	0	0		1,00000	0,34957	-16,01492		93.45	16.15	44.57	15785.1	0.05700
H,C., -0,S(0)0R	ن	.0.72457	c	c	e	-152.34026	0.91771	0.87495	.15,53033	-15.33946	95.98	14.02	46.10	1,25319	0.09112
0,5(0)0R'	o'	-0,W26WB .	41.46459	ď	0 .		1,00000	0.84418	-16.11722		94.30	15.30	44.80	127343	0.06624
RH,C, -0,5(0)OR'	ن	-0 82688	-0.92918	0	0	₹וזנגנצו.	0,9171	0.12053	-16,58181	-1639093	92.41	17,59	43.35	1.30512	0.03456
с-н (сн.)	ù	*16Z6'0-	•	С		-152.54487	17716.0	0.16359	-15.75493	-15,56407	77.49	102.51	41.48	1,23564	Q.18708
C-H (CH <sub>3</sub> )	L	10,92918	-0.9291X	c	•	-153.47406	0.91771	0.81549	-16.68412	-16.49325	68.47	111.53	35,84	135486	0.29933
C - H (CH)	i	0.92918	.0.9291R	- 0.92918	0	-154,40324	0.91771	0.77247	-17.61330	-17.42244	61.10	118.90	31.37	1.42988	0.37326
H,C,C,H,C'H, -	٠	.0.9291g	. 0	c	. 0	-152.54487	0,91771	Q.R6359	-15.75493	-15.56407	ra.rs	116.18	30,08	1.13779	0.38106
H,C,C,H,C'H, – (C – C' (a))	ť	1 -B.92913	81¢ <u>5</u> 0.0-	· a	0	-153,47406	0.91771	0,41549	-16,63412	-16,49325	56.41	123.59	30.06	1.90820	0.45117
R-H,C,C,(H,C,-R)HCH,-	ť	RIOZOD	*1050.0-	21676'0"	0	-134,40524	0.91771	0.77247	-17.61330	-17.42244	48.30	02'161	21.90	1.97162	0.51388
$h - H_{\mathcal{L}_{*}}(R - H_{\mathcal{L}_{*}})C_{*}(R' - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} - H_{\mathcal{L}_{*}})(H_{*})(H_{*} - H_{\mathcal{L}_{*}})(H_{*} (H_{*} - H_{\mathcal{L}_{*}})(H_{*})(H_{*} - H_{\mathcal{L}_{*}})(H_{*})(H_{*} - H_{\mathcal{L}_{*}})(H_{*})(H_{*})(H_{*} - H_{\mathcal{L}_{*}})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_{*})(H_$	1.	-0.9291K	-0.72457	-0.72457 .	-0,72457	-154.71860	0.91771	0.75819	-17.92866	-17,73779	48.21	£7.161	21.74	1.95734	0.50370
lxof',C,(H,f',-R')HCH,-	.,	A1029.D-	-0.92918	81676'O	0	-154.40324	0.91771	0.77247	-17,61330	-17.42244	48.30	131.70	21.90	1,97162	0.51358
lerK" (K-H;C;)C, (K-H;C;)CH2- (C-C (c))	ن ٔ	7817.0-	-0.72457	. 40.72457 ·	-0.72457	-154.51399	0.91771	0.76765	-17.92866	QTT.T.T.1-	50.04	96'611	. 9972	1.94462	0,47298
((, - ', (j)) ien(, ', (H, ', ', - n') H(H, -	٠,	25r72 D-	-0.92918	-0.925fx	Ġ	-154.19863	17710.0	0.78155	-17.40869	-17,21783	52.7R	17.73	24.04	1,92443	0.47779
$knC_{*}(R'-H_{2}C_{*})C_{*}(R'-H_{2}C_{*})CH_{2}-$ (C'-C' (f))	رڙ.	0,72457	- 72457 0-	. 72457 n.	72457 n.	-134.51399	17716.0	0.76765	-17,92866	-17.73770	\$0.04	129.96	22.66	1.94402	0.47298

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	0.5	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
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- 5	0.85395	0.85395	_	1.20632	0,91771	0.91771	. 0.91771	0.91771	17710	0.91771	0.91771	14416.0	17716.0
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ر: ا	0.5	0.5	0.5	0.5	0.75	0.75	0.75	5.0	0.5	5.0	0.5	5.0	0.5
	-	-	0.77641	_	-	-	-	_		-	-	1	-
V, (aV)	-33,15757	-33.47304	-48.93512	-82,65003	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.101.12	-29.10112
7, (aV)	10.12103	10.15605	9.18680	19,31325	38,92728	25.78002	12.87680	9,33352	9,33552	9.37275	9,33352	5.37275	9.37273
T (cV)	9.17389	9,32537	14.36741	20.81183	32.53914	21.06675	10.48582	6.77464	6.77464	00806'9	6.77464	6.90500	6.90500
V. (uV)	4.58695	-4.66268	-7.18371	-10,40592	-16,26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3,38732	-3.45250	-3.45250
E(.n no) (eV)	-14.63489	-14.63489	0	-11.52126	-15.56407	-15.56407	-14.63489	-15,56407	-15.56407	-15,35946	-15,56407	-15,35946	-15.35946
46 (12) (an or) (al)	-1.44915	-1.65376	-0.92918	-1.16125	0	0	0	0	0	0 .	0	0	0
Et (so so) (cV)	-13.18574	-12.98113	0.92918	10095.01-	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
E, (n, 200) (cV)	-31.63533	-31.63544	-31.63543	-63.27088	-67.69451	-49.66493	-31.63533	-31.63537	-31,63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_r(atuni - atom, nisp^2 AO)$ (cV)	-1.44915	-1.65376	-0.92918	0	0	0	0	-1.85836	-1.85836	-1.44915	-1.85836	-1.44915	-1.44915
E, (se) (eV)	-33,08452	-33.28912	-32,56455	-63.27074	-67.69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
@ (10" rad/s)	22.0240	12.1583	33,4164	17.6762	24.9286	24.2751	24.1739	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
E. (0V)	14,49660	8,00277	21.99527	11.63476	16.40846	15.97831	15.91299	6,21159	621159	10.19220	6,21159	6.29021	6.29021
E, (eV)	-0.24921	-0.18631	-0,30214	-0.21348	-0.25352	-025017	-0.24966	-0.16515	-0.15515	-0.20896	-0.16515	-0.16416	-0.16416
Esm (cV)	0.13663	0.13663	0.08679	0.12832	0.35532 (Eq. (13.458))	0,35532 (Eq. (13.458))	0,35532 (Eq. (13.458))	0.12312 [2]	0.17978	0.09944	0.12312 [2]	0.12312 [2]	0.12312 [2]
E (eV)	-0.18089	-0.11799	-0.25875	-0.14932	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10339	-0.10260	-0.10260
E_ (eV)	0,14803	0.14803	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Er (num) (cV)	-33,26541	-53.40711	-32,82330	-63.56937	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	+33.24376	-33.59732	-33,18712	-33.18712
E (4, so in) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489
Enter la so no) (eV)	0	0	0	-1.16125	-13,59844	-13.59844	-13.59844	٥	.0	0	0	٥	٥
E 10_ (aV)	59500 £	4.13733	3.55352	3.86856	12.49186	7.83016	332601	4.32754	4.29921	3,97398	4.17951	3.62128	3,91734

Table 15,181. The total band energies of alkyl sulfrest calculated using the functional group composition and the energies of Table 15,180 compared to the experimental values 131.

Formula Name C-O (i) C-O (ii) O-S SO (.H, (.H, C.H, C.H, C.-C. (a) C-C. (b) C-C. (c) C-C. (d) C-C. (d) C-C. (e)

	Frm A		;				107	(propane)	(porogene)	(isobutano)	0.111.0 (buczne)	(isobutane)				110.8	(aurinocu)		111.4	111.4	(Gopfidane)
	Cal A	0	:	25.85	103.35	17.84	77 80		110.49		110.49		100,50	100.44	109.44	19.011	110.76		111.27	11.3	
	-	" <b>©</b>	=						_						Γ			1			
	-	•	>					1							Γ					T	
	9	· =	?						15.69		1569			70.56	70.56						
,40).	12	. §		.1,65376	-1.63376	-0.72457	•						c			-1.65136	0		0	-1.85836	
– аюн, тяр	ۍ	•		Q. RAK35	0.84418	0 82000	1.15796						1.157%			0,818,0	(,Duter?)		1,048#7	L.DARR7	
s Er(aiam	٢			-	-	-	6.73		-	1	-		6,3			-	6.33		0,75	0.75	
used. E, i	ن	•		-	-	0,77641 (Eq.	(13.139)	1	<del>**</del>	1		Ţ.	-			_	-	T	-	-	1
gangle were	ئ			-	-	-	-					-	-			<del>-</del> .	0.75		۲.	0.75	1
m the preceding	ა'	Atom 3		0.844JR	0.K4418	0.77641 (Eq. (15.139))	-									0,11549	0.91771		17116.0	17716-0	
arameters fro	ۍ.	A		0.85252	0,8441K	0.86359	0.167599					0 174160				0.81549	0.87493		0.87495	0.87495	
Assessed and the parameters of any) summer and experimental values [1]. In the calculation of \$\theta\$, the parameters from the proceeding angle were used. \$\textit{E}_t\$ for an = atom, may? AO	Atom 2 Hybridizerion	Designation	(Table 15.3.A)		=	8	Ξ.					=				a	_		-	-	
In the calcu	£,000	Alran 3		0,0	.0	10.36001	, =		-			=				-16.68412 C.	-N.82575	-14,12575	٠,	-14.8333 C.	
mental values [1]	Atom I Itsbridization	Occignation	(Table 15.3.A)		=		,					_				2	ŗ		~	3	
es und exper	I'r			-15.95954	-16.17 <u>11</u>	-13.75493	-15,75493					-15.75493			211113	-10.fb#41.2	-15.55B33	-15.55033	ئن	-15.55033	
any sulli	Terrana	Aims (ap)		TUGU"	92H97+	91MC+	3,4253	L				3,4252				4.7958	4,1633		4. lb33	4.7952	
i all rection of	ž	(e)		2.96203	1,96203	2,96203	211106					1.00711				2.91547	2.11323		7,000	77806.7	
1	7	(°°)		2.11.72	2,06203	3.68KG2	211106					2,09711				2.91547	2.91547	101647		2.90327	
Alteretal Americ				05'07 :	, CO <sub>2</sub> , SO <sub>2</sub>	s'0.37	Mathian ZMC, H		ת "נינ"	-	H'.5".)7	Math.l ZHC H	70.07	H.J. 37	7.57	, J. 4.	H. J. J.	H*.5*.17	, ) mi	۳۰ را ۲۰ راز را	לנ"נ".

SULFATES  $(C_n H_{2n+2}(SO_4)_m, n = 2,3,4,5...\infty)$ 

The alkyl sulfates,  $C_nH_{2n+2}(SO_4)_m$ , comprise a  $C-O-SO_2-O-C$  moiety that comprises two types C-O functional groups, one for methyl and one for alkyl, and O-S and  $SO_2$  functional groups. The alkyl portion of the alkyl sulfate may comprise at least two 5 terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in sulfates are equivalent to those in branched-chain alkanes.

The methyl and alkyl C-O functional groups having  $E_T(atom-atom,msp^3.AO)=-1.44915\ eV$  and  $E_T(atom-atom,msp^3.AO)=-1.65376\ eV$ , 15 respectively, are equivalent to the corresponding groups given in the Sulfites section. The O-S functional group having  $E_T(atom-atom,msp^3.AO)=-0.92918\ eV$  is equivalent to that given in the Sulfites section. The  $SO_2$  functional group is equivalent to that of sulfones with  $E_T(atom-atom,msp^3.AO)=0$  as given in the Sulfones section.

The symbols of the functional groups of branched-chain alkyl sulfates are given in Table 15.183. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl sulfates are given in Tables 15.184, 15.185, and 15.186, respectively. The total energy of each alkyl sulfate given in Table 15.187 was calculated as the sum over the integer multiple of each  $E_D(cong)$  of Table 15.186 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl sulfates determined using Eqs. (15.79-15.108) are given in Table 15.188.

A transfer of the second of the control of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second of the second o

		-	Group Group	2.12499 3.12409	-		
			Group	1.67465	1 05561	1.11827	
		(110) 11.0	Grom	1.67122	1.05553	1,11713	1 107
•		(12) 11-0	Group	1.64920	1.04856	1.10974	1.107
SO, SO, CO - SO, CO - SO, CO - SO, CO - H - CO - CO - H - CO - CO - CO - C		SO,		1,85851	1,36327	1,44282	1 / 72
00-5 0-1 0-1 0-1 0-1 0-1 0-1 0-1 0-1	(E) (E) (E) (E) (E) (E) (E) (E) (E) (E)	able 13.184. The Ecometrical bond parameters of alkyl sulfates and experimental values (1) $C = O(1)$ $C = O(1)$ $O = S$ $SO$ ,		1.70299	1.48102	. 1.56744	
		bond parameters of a	Group	1.79473	1.33968	1.41785	
پُرِيُ پُرِي	Q.	C-0 (i)	dhou	1.80717	1,34431	1.42276	
O-SO, SO, CH, group CH, group CC bond (n-C) CC bond (in-C) CC bond (in-C) CC bond (in-C) CC (iso in-C) CC (iso in-C)	CC (tro t-C)	Parameter	,	0 (0°)	(0)	Bond Length 2c' (A)	Exp.

Table 15.183. The symbols of functional groups of alkyl sulfates. Functional Group Group Group Symi

		_	т		т	_		_		_	_	-	_	_	-
	0-2-0	Group		2.10725	1 16121	+016+		ccore.		1.532	(propane)	1551	(butane)	03203	1.36130
	(e) C-C (e)	Group		2.10725	1 45164	5100	1 50,000	55055.1		1.532	(propane)	1.5	(butane)	1 42740	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,
	(P) 2-2	Group		2.12499	1.45744		1 54780	200		1.532	(propane)		(Out thic)	1.54616	
	(a) <u>J</u> – J	e e	2 16776	4.107.23	1.45164		1.53635			1.532	1 531	(Austral)	(company)	1.52750	
	(a) U-U	· dinoro	2 12400		1.45744		1.54280			1.532	1531	(buttere)		1,54616	20,00
	(c) (a)	dans	2.12499		1.45744		1.54280		-	(propage)	1.531	(butane)		1.54616	007070
ı	Group	ł	1.67465		1.0560.1		1.11827			1.122	(isobutane)		1.000	1,277.24	0.63095
, , e	C-H (CH;)	Group	1.67122	1,06657	0.0000.1		1,11713		1 107	(C-H propane)	1.117	(C - M butane)	1 10560	incre.	0.63159
(1,0)	('H') H - 1	dioio	1.04856				1.10974	·	1.107	(C-H propane)	1.117	(etamo u - )	1 27795		0.63580
so.			1.83851	: 1,36327			1,44282			(dimethyl		İ	1.26315	1000	0.72333
0-5		Toplow 1	1.70299	. I.48102			. 1.56744			1.574	1,42,500		0.84069	O PKDKK	2000
(E) 0-3	Group	17,07	2000	.1.33968			1.41785						1.19429	0.74648	
	Group	1.80717		1,34431			9/2741						1.20776	0.74388	
נייישמובופר		0 (0,)		c. (a.)	Bond	Lenrih	5c. (4)	ä	Bond	Length	ट	-	(") (")	. 5	

					1			-							
המעק	Atom	ئ	· .	E,	, <sub>t</sub>	Final Lotal	, J	1	Contract	$E(C2sp^3)$	.6	6	6	7	9
,		(cV)	(eV)	(cV)	(eV)	2 to 12	(°)	(°)	(cV) Final	(S)	<u> </u>	©	0	(°)	(°)
						(eÝ				rmal					
(RO), (O, 15 = O.	8	0	. 0	-0.46439	-0.46459 .		1.32010	0,86359	-15,75493		95.46	19.54	43.13	1.35635	0.00693
(RO); (O,)S = O,	0,	Q	0	0 · ·	. 0		1.00000.	17716.0	-14,82575		95.05	\$6,95	46.36	1.28256	0.08071
CH,0, - S(O,)OR	S	-0.46459	-0.46459	ņ	0		1,32010	0,86359	-15.75493		126.68	51,32	55.47	0.96521	0.51581
$CH_{,O_{\bullet}} - S(O_{\bullet})OR$	'n	-0.46459	-0.72457	0	0		000001	0.84957	-16.01492		126.03	51.97	24.81	0.98133	0.49969
$RCH_2O_a - S(O_2)OR^{-1}$ $(C - O_1(i))$	o*	-0,46459	-0.82688	0			1.00000	0.84418	-16.1772		T.25.TT	5423	57.56	0.98753	0.49349
$H_1C_* - O_*S(O_*)OR$ (C - O (i))	ω"	-0.72457	-0.46459	0	. 0	•	1.0000	0.94957	-16.01492		93,85	\$1.08	44,57	1,28731	0.05700
H,C, -O,S(O,)OR (C-O (i))	3	-0.72457	0	υ .	. 0	-15234026	17716.0	0.87495	-15.5503	-15.35946	95.98	84.02	46.10	6182.1	0.09112
$RH_1C_1 - O_4S(O_2)OR$ $(C-O_1(i))$	0.	-0 \$2688	-0.46459	0	0.		1.0000	0,84418	-16.11722		94.30	<b>15.</b> 50	44,80	1,27343	0.06624
RH,C, ~ O,S(O <sub>2</sub> )OR' (C, ~ O (ii))	ຸ່ບ້	-0.8268R	-0.92918	0	0	27172.81.	0.91771	0.82053	-16,58181	-16.19095	92.41	87.59	40,35	1,30512	0.03456
C-H (CH,)	ر.	-0.92918	0	0	0	.152.54487	0 91771	0.86359	-13,75493	-13,56407	77.49	102.51	41.48	1.23564	0.18708
$C-H$ $(CH_1)$	Ü	-0.92918	-0.92918	0	0	153,47406	17719 0	0.81549	-16.68412	-16.49325	68.47	11,53	35.84	1,35486	0.29933
с. – н (сн)	ij	-0.92918	-0.92918	0.92918	0	154 40324	17719.0	0.77247	-17.61330	-17,42244	61.10	118.90	76.16	1,42988	92575.0
H,C,C,H,CH, - (C,-C, (a))	ij,	91626.0-	0	0.	. 0.	-152.54487	0.91771	O.R6339	.15.75493	-15.56407	53.82	116.18	30.08	1.83879	0,38106
$H_iC_iC_iH_jCH_i-$ (C=C (a))	C,	-0.9291B	-0.92918 .	0 .	0 .	-153.47406	17716.0	0.81549	-16.68412	-15.49325	56.41	123.59	85.08	06806.1	0.45117
$R - H_1C_2C_1(H_2C_1 - R^1)HCH_1 - (C^2 - C^2)$	3	-0.92918	\$1625.0	-0.92918	0	-154 40324	0.91771	7x277.0	-17.61330	-17.42244	48.30	07.161	21.90	1.97162	0.5 388
$R = H_2C_2(R^2 + H_2C_2)C_3(R^2 + H_2C_2)CH_2 - (C - C_2(c))$	ڻ'	81626.0-	-0.72457 .	-0.72457	-0.72457	154.71860	0,91771	0.75889	-17.92866	-(7.73779	48.21	131.79	21.74	1.95734	0.505.0
$isaC_{\mu}C_{\mu}(H_{\mu}C_{\mu}-H^{\mu})HCH_{\mu}-(C_{\mu}-C_{\mu}(\Phi))$	:3	-0.92918	81929.0-	-0.92918	0.	-154.40324	0,91771	0.77247	-17.61330	-17.42244	48.30	02.161	21.90	1.97162	0.51388
(C-C')	<b>.</b>	-0.72457	-0.72457	-0.72457	-0.72457	-134.51399	0.91771	0.76765	-17.92866	-17.73779	\$0.04	129.96	9971	1.94462	0.49298
$tert'_{s}C_{s}(H_{s}C_{s}-R)HCH_{s}-(C-C^{*}(9))$	ن	-0.72457	-0.92918	-0.92918	.0.	-154.19263	0,91771	0,74155	-17.40\$69	-17,21,783	52.78	27.11	24.04	1.92443	0,47279
$h_{KOC_{\sigma}}(R^{-} + H_{1}C_{\sigma})C_{\sigma}(R^{-} + H_{2}C_{\sigma})CH_{1} - (C - C^{-}(1))$	ų,	-0.72457	-0.72457	-0.72457	-0.72457	-154.51309	17216.0	0.76765	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.185. The MO to HO intercept geometrical bond parameters of alkyl sulfates. R,R',R'' are H or alkyl groups.  $E_{\bf r}$  is  $E_{\bf r}$  (atom – atom, msp. AO).

Table 15.186. The energy parameters (eV) of functional groups of alkyl sulfates.	ters (eV) of functi	onal groups of alk	vi sulfatės.										
Parameters	(E) 0-10	(i) 0-0 0-0	S-0	SO.	. H.	: HJ C	Croup Group	Graup	Group Group	(a) (b) (c) (d) (d) (d) (d) (d) (d) (d) (d) (d) (d	Green Green	Group	Group Group
	-	ing.	-	dino.	Croup	Cranb.		-	-				-
	-	-	-	•	,	,	-	-	,		-	-	
$n_{\mathbf{i}}$	0	0	0	0	2	_	0	c	0	0	0	0	0
'u'	0	0	0	0	0	. 0	0	. 0	0	0	0	0	0
. G	0.5	5.0	0.5	5.0	54.0	0.75	0.75	0.5	5'0	5'0	\$0	5.0	0.5
C.	-	_	0.77641	_	-	-	1	-	-		-	1	-
ક	-	-		-	_	-	-		-	-	-	_	-
	0.85395	0.85395	-	1,20632	0.91771	17716.0	17716.0	111160	17716.0	0.91771	0.91771	17716.0	0.91771
5	0	0	0	1	0		1	. 0	0	0	1	1	0
· c'	2	7	2	8	_	1	1	2	2	2	2	2	2
5	0	0	0	_	£	2	-	0	. 0	0	0	0	c
ر:	0.5	0.5	6.0	5.0	. 57.0	0.75	0.75	0.5	50	5.0	5.0	0.5	0.5
 ن:	1	-	0.77641	_	-	-	1	-	1	-	-	-	-
V, (aV)	-33.15757	-33.47304	-48,93512	-180,36454	-107.32728	-70,41425	-35,12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (aV)	10,12103	10.15605	9.18680	39.92103	38.92728	25.78002	12.87680	9.33352	9.33352	9.37273	9.33352	9.37273	9.37273
T (eV)	9.17389	9.32537	14,36741	48,52397	32.53914	21.06675 .	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V. (aV)	-4.58695	4.66268	.7.18371	-24.26198	-16.26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(+0 10) (aV)	-14.63489	-14.63489	0	-11.52126	-15.56407	-13,56407	-14,63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15.35946
DE use (or m) (cV)	-1.44915	-1.65376	-0.92918	-1.16125	0	0	. 0	0	0	0	0	0	0
Ex (40 m) (eV)	-13.18574	12,98113	0.92918	-10,36001	-15,56407	-15,56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15,35946
. (E, (n, m) (c/)	-31,63533	-31.63544	-31.63543	-126.54154	-67.69451.	-49.66493	-31.63533	-31.63537	-31.63537	-31.63535	-31.63537	-31.63535	-31.63535
$E_r(alom - alom, msp^3, AO)$ (eV)	-1.44915	-1,65376	-0.92918	0	. 0	0	0	-1.85836	-i.85836	-1.44915	-1.85836	-1.44915	-1.44915
F. (110) (aV)	-33.08452	-33.28912	-32.56455	-126.54147	-67,69450	-49.66493	-31.63537	-33.49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
$\omega \left(10^{15} rad / s\right)$	22.0240	12.1583	33,4164	11.5378	24.9286	24.2751	24.1759	9.43699	9.43699	15.4846	9,43699	9,55643	9.55643
Er (aV)	14,49660	8.00277	21.99527	7.59437	16.40846	15.97831	15.91299	6.21159	6.21159	10.19220	6,21159	12062-9	6,29021
$\vec{E}_{D}$ (cV)	-0.24921	-0.18631	-0.30214	-0.17247	-0.25352	-0.25017-	₼.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
ELIN (OV)	0.13663	0.13663	0.08679	0.12832	0.35532 (Eq. (13.458))	0,35532 (Eq. (13,458))	0,35532 (Eq. (13,458))	21521.0	0.17978	0.09944	0.12312	0.12312 [2]	0.12312
E., (eV)	-0.18089	-0.11799	-0.25875	-0.10831	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
King (eV)	0.14803	0.14803	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Kritimal (cV)	-33.26541	-33.40711	-32.82330	-126.97472	- 67.92207	-49.80996.	-31.70737	-33.59732	-33,49373	-33.24376	-33.59732	-33.18712	-33.18712
Bun, (4, 11'10) (eV)	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489
Erryl, wind (cV)	0	0	0	-1.16125	-13,59844	-13.59844	-13.59844	0	0	0	0	0	0
$E_{D}(\omega_{m})$ (cV)	3.99563	4.13733	3.55352	8.61994	12.49186	7.83016	3,32601	4.32754	4.29921	3.97398	4.17951	3.62128	3.91734
								:					

(a) C-C(b) C-C(f) Table 15.187. The total bond energies of alkyl sulfates calculated using the functional group composition and the energies of Table 15.186 compared to the experimental values [3].

Formula Name C - O (i) C - O (ii) O - S SO; CH; CH; CH C - C (a) C - C (b) C - C (c) C - C (d)

Group Group Group

	Exp. 8		120.9 [44] (dimethyl sulfate)	109.67 [44] (dimethyl sulfare)	(6methyl sulfite)	i17.43[44] (dimethyl sulfate)	. 107 . (propenc)	112 (propana) 113.8 (butaro) 110.8 (resbutane)	111.0 (buttere) 111.4 (isobutere)				110.8 (isobutane)		111.4 (isobatane)	111.4 (fsobutane)	
	<u></u>		120.44	110.26	103.35	117.84	108.44	110.49	110.49	109,50	109,44	109.44	110.67	110.76	111.20	11.37	107.50
	θ, ©																
	6 O	:					,			_	_						
	0, ©	:						15.69	69.51		70.56	73.55					2 2
.40).	(e.V.)		-1.65376	97889.1-	-1.65376	-0.72457	0			0			-1.85836	٥	•	-1.85836	
– atam, msp	٧.		0.85252	0.84815	0.84418	0.81000	1.15796			1.15796			0.21549	1.04887	1,04887	1.04887	
is E <sub>T</sub> (atom	ئ		. <b>-</b>		-	-	0.75			0.75			-	67.0	0,75	27.0	
e used. Br	ບ້		-	-	-	0.77641 (Eq. (15.139))	_			-			-	-	~	-	
gangle wer	. ت			1	-	_	-			-			-	0.75	0.75	27.5	
the precedin	Cy Almai 3		0.85252	0.84418	0.84418	0,77641 (Eq. (15.139))	-			<u>-</u> `			0.81549	17716.0	17716.0	0.91771	
urameters from	C <sub>3</sub>		0,85232	0.65252	0,84418	0.86359	0.86359			0.86359			0.81549	0.87495	0.87495	0,87495	
listion of $\theta_{\rm r}$ , the pa	Afom 2 Hybridization Designation	(Table 15.3.A)	. 6	=	=	s	н		•	×			25	_	-	-	
. In the calcu	Alema 2		-15.95954 O <sub>A</sub>	-16.1172 O	-16.1172	-10.3600! .N	ж		·	н			-16.68412	-14.62575 C.	-14.82575 C <u>.</u>	-14.82575 C.	
nental values [1]	Atom I Hybridization Designation	[Toble 15,3.A]	0	o	=	,	,						33	~	5	~	
s and experi	Ana i		.15.93934	7) 7)	.16.11722 .0	-15 75493	-15.75493			-15.75493			-16.68472	".) 11855.21-	-15.55033 C.	-13.55033 C <sub>4</sub>	
alkyl sulfate	2c' Tonimal Avins ( Q. )	,	4,7329	4.6690	4,6476	4 8416	3.4252			3,4252			4,7958	4,1633	4,1633	4,7958	
ameters of	2¢, [a]		2,72654	1.96103	1,06203	1,96203	2,11106			112607			2.91547	2,11323	2.09711	7,109,17	
nd angle pa	2c' !head ! ( o, )		2,72654	2.77654	2.96203	2,68862	2.11106			112607			291547	2.91547	2.91547	7.50327	
Table 15.188. The bond angle parameters of alkyl sulfates and experimental values [1]. In the calculation of $\theta_c$ , the parameters from the preceding sugle were used. $S_r$ is $E_r$ (arom - arom, may 7.40)	Alman III Angle		'08'07	`os"07	'os'oz	s'o".>7	Meth bra ZHC, H	: '5'5'57	н'з'.х	Metal ZHC, H	, ZC, C, C	H1.5.37	20,7,7,7,7 to C,	7.5°.7H H. 5'.57	ZC,C,H In C,	ופו כ" רכ"כ.'כ.'	70.0.7

NITROALKANES 
$$(C_n H_{2n+2-m} (NO_2)_m, n=1,2,3,4,5...\infty)$$

The nitroalkanes,  $C_n H_{2n+2-m}(NO_2)_m$ , comprise a  $NO_2$  functional group and a C-N functional group. The alkyl portion of the nitroalkane may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and 5 methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in nitroalkanes are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^22s^22p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  ${}^3P_2$ . The electron configuration of nitrogen is  $1s^22s^22p^3$ , and the orbital arrangement given by Eq. (10.134) has 15 three unpaired electrons corresponding to the ground state  ${}^4S_{3/2}^0$ . The bonding in the nitro  $(NO_2)$  functional group is similar to that in the  $SO_2$  group given previously. It also has similarities to the bonding in the carbonyl functional group. In the  $NO_2$  group, the two unpaired electrons of the O atoms form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a linear combination of two bonds, each of bond order two involving the 20 nitrogen AOs and oxygen AOs of both oxygen atoms. The nitrogen atom is then energy matched to the  $C2sp^3$  HO. In nitroalkanes, the  $C2sp^3$  HO has a hybridization factor of 0.91771 (Eq. (13.430)) with a corresponding energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)), the N AO has an energy of  $E(N) = -14.53414 \, eV$ , and the O AO has an energy of  $E(O) = -13.61806 \, eV$  [38]. To meet the equipotential condition of the union of the N = O the N = O-bond MO given by Eqs. (15.68) and (15.70) is

$$c_{2}(O \text{ to } N2p \text{ to } C2sp^{3}HO) = \frac{E(O)}{E(N)}c_{2}(C2sp^{3}HO)$$

$$= \frac{-13.61806 \text{ eV}}{-14.53414 \text{ eV}}(0.91771)$$

$$= 0.85987$$
(15.140)

Since there are two O atoms in a linear combination that comprises the bonding of the  $NO_2$  group, the unpaired electrons of each O cancel each others effect such that  $E_{mag}$  is not subtracted from the total energy of  $NO_2$ . Additionally,  $E_T(atom-atom, msp^3.AO) = -3.71673 \, eV = 4(-0.92918 \, eV)$  (Eq. (14.513)) is the maximum given the bonding involves four electrons comprising two bonds, each having a bond order of one.

The C-N group is equivalent to that of primary amines except that the energies corresponding to vibration in the transition state are matched to a nitroalkane and  $\Delta E_{H_2MO}(AO/HO) = -0.72457 \ eV$  for nitroalkane and  $\Delta E_{H_2MO}(AO/HO) = -1.44915 \ eV$  for primary amines. Whereas,  $E_T(atom-atom,msp^3.AO) = -1.44915 \ eV$  for both functional groups. This condition matches the energy of the C-N group with the  $NO_2$  having  $\Delta E_{H_2MO}(AO/HO) = 0$ .

The symbols of the functional groups of branched-chain nitroalkanes are given in Table 15.189. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and 15 energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of nitroalkanes are given in Tables 15.190, 15.191, and 15.192, respectively. The total energy of each nitroalkane given in Table 15.193 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.192 corresponding to functional-group composition of the molecule.  $E_{mog}$  given by Eq. (15.58) was subtracted for each t-butyl group. The bond angle parameters of nitroalkanes determined using 20 Eqs. (15.79-15.108) are given in Table 15.194.

Table 15.189. The symbols of functional groups of nitroalkanes.

Functional Group	Group Symbol
NO <sub>2</sub> group	$NO_2$
C-N	C-N
CH <sub>3</sub> group.	$C-H$ $(CH_3)$
CH₂ group	$C-H\left(CH_{2}\right)$
СН	C-H
CC bond (n-C)	C-C (a)
CC bond (iso-C)	C-C (b)
CC bond (tert-C)	C-C (c)
CC (iso to iso-C)	C-C (d)
CC (t to t-C)	C-C (e)
CC (t to iso-C)	C-C (f)

C-C (f) Group	2.10725	1,45164	1.53635	1.532	(propune)	1.531	(butzne)	1.52750	0.68888
C-C (e) Group	2.10725	1,45164	1.53635	1.532	(propane)	1.531	(butane)	1.52750	0.68888
C-C (d) Group	2.12499	1.45744	1.54280	1.532	(aurdoad).	1.531	(butune)	1.54616	0.68600
C - C' (c) Group	2.10725	1.45164	1,33635	1.532	(propare)	1.531	(butzne)	1.52750	0,68888
Group	2.12499	1.45744	1.54280	1.532	(propane)	1.53	(batane)	1,54616	0.68600
C'-C'(a) Group	2.12499	1.45744	1.54280	1.532	(propane)	1.531	(butane)	1.54616	0.68600
Group	1.67465	1,05661	. 11827		1.12	(isobutane)		1.29924	0.63095
('-H (CH <sub>1</sub> )	1.67122	1.05553	1,11713	1.107	(C - H propane)	1.117	(C - H butane)	1,29569	0.63159
C-H (CH,) Group	1.64920	1.04856	1.10974	1.107	<u></u>		<u>ء</u>	1,37295	0.63580
C-N Group	1.97794	1.40639	1.48846		1.489	(nitromethane)		1.39079	0.71104
<i>NO</i> ₃ Group	133221	1,15421	1,22157		1.224	(nitromethane)		0.66526	0.86639
Parameter	0 (a,)	c. (a,)	Bond Length 2c' (A)	Fyn Bond	- Frint		<u> </u>	h.c (a)	ď

Table 19,131. The WO to the body but the body			integral integrations. At								İ				
Bond	Atom	E,	E,	F.	r.	Final Total	1,8	٤,	Ecnston	E(Czp')	.6	j <sub>0</sub>	6.	9	ď,
		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	C'2vp' (eV)	(°)	(°)	Final Final	(eV)	£		c C	(°)	<b>b</b>
RN(O) = 0	9	O.92918	a	=	c		1,00000	0 86359	-15.75493		135.25	44.75	50.50	0.54089	0.61333
RN(0) = 0	>	81626.0	HIUZU.D.	-0.72457	a		0,93094	0,78155	-17.40x69		131.57	48.43	05'19	0.63558	0,51864
H,C-NO.	i	-0.72457	c	c	0	-152,34026	17710,0	0 87495	-15.55033	-15.35946	80,47	99,53	38,35	1,5123	0.14484
$RH_2C-NO_2$ $R=H_2dkyl$	2	ж1629.13-	-0.92918	- 41,72457	0		HEDEG'O	0.78155	-17.40869		69.30	110.70	31.71	1,64259	0.27/520
-H,C, - NO.		40,72457	-0.9291R	0	e .	-153,26945	17710.0	0.R2SG2	-16.47951	-16.21864	74.96	105.04	34.98	1.62061	Q21422
C-H (CH,)	j.	K1020,0-	C	0	c	-152.54487	17710.0	0.86359	-15.75493	-15.56407	77.40	15.201	41,43	1,23564	n.1870x
('-H (cH;)	ij	-0.9291R	-0.9291x	0	o.	-153.47406	17716.0	0.81549	-16,68412	-16.49325	68.47	111.53	35.14	1334%6	0,29933
(-H (CH)	r.	40,92018	#16Z6'U-	-0.9291R	0	-154.40324	144160	0.77247	-17.61350	-17,42244	61.10	118.90	31.37	1,42988	0,37576
H,C,C,H,CH <sub>2</sub> – (C'-('a))	ن	R1020,0-	0	9	u	-152,54487	17716.0	0.84359	.15,75473	-15,36407	63.12	116.18	30.08	1,53879	0.38106
$H_1^{C}(\mathbb{C},H_1^{C}(\mathbb{H}_3-\mathbb{C}))$	٠,٠	H1020,0-	#1626'0-	0	0	-153,47406	12216'0	0.R1349	-16.68412	-16.49325	56.41	123.59	26.06	1.90830	0.45117
$R - H_2C_*C_*(H_2C_* - R^*)HCH_3 - (C^* - C^*)b$	ن	#I026;0+	-0.9291X	41626.0-	0	-154,40324	12216'0	0,77247	-17,61330	-17.42344	48.30	131.70	21.90	1,971@	0.51388
(C'-C', (C'))	ť	-0,92918	. 7242T.D.	-0.72457	151457.0.	-154.71x60 -	12216.0	0 75RH9	-17.92866	677.71-	48.21	131.79	21,74	1,95734	0.50570
$iso(`, C', (H_2C', -R')HCH_2 - (C', -C', (d))$	٠,	-0.92918	-0.92918	-0.92918	D	NZ611+'HS1-	122160	0.77247	-17,61330	-17,42 <u>2</u> 844	48,30	131.70	21,50	1,97162	0,5138R
10TK. (R-H;C,)C. (R-H;C,)CH; -	ڻ	-0.724 <i>S</i> 7	. 18421.0-	-0.72457	12.157	מננוצ ויין י	17716.0	0.76765	-17,92866	.17.73779	30.04	96:621	22.66	1,94462	0.49298
ופעת "נ" (H'נ" - H) אנא" -	ť	7245T.O-	#16Z6'0*	ж1626 0-	.0	-154.19KG	122160	0.7k155	-17,40869	-17.21783	52.7k	22.721	24.01	1,92443	0.47279
$(uoC_*(R'-H_2C_*)C_*(R''-H_2C_*)CH_2 - (C'-C'(f))$	ر.'	-0.72457	151710-	-0.72457	15457.0-	15431399	12161	0,74765	-17,92866	91757.71-	50.04	129.96	22.66	1.54462	0.49298

Famelore	ArO <sub>2</sub> Group	Ω−Ω Group	Parameters M/2, C-N CH, Group Group	C.H.1 Group	Group	Group	CC (b) .	C ~ C (c) Group	C-C (d) Group	Group	Greup
7,1	~	-	3	r	1		1	1	1	1	1
ž,	٥	0	2	-	۰	0	. 0	0	0	0	0
ž.	0	0	0	0	0	0	0	0	0	0	0
	0.5	0.5	0.75	0.75	0.75	0.5	5.0	0.3	0.5	0.5	0.5
	-	-	-	_	-	-	-	1	1	1	
		-	_	-	-	-	1	1			1
	0.85987	0.91140	17716.0	0.91771	17716.0	0.91771	0.91771	12216'0	17716.0	17716.0	14160
-5-	0	o	G	_	-	0	0	0	1	1	0
.5	4	2	-	-	_	2	2	2	2	2	2
	0	0		2	-	0	0	0	0	0	0
	0.5	0.5	0.75	0.75	0.75	0.5	5.0	6.5	0.5	0.5	0.5
ئ	-	-	-	-	_	_	-	-	-	1	1
V, (eV)	-106.90919	-31.36351	-107.32728	-70.41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29,10112	-29.10112
V, (eV)	23,57588	9,67426	38.92728	23.78002	12,87680	9,33352	9.33352	9.37273	.9.33352	9.37273	.9,37273
T (eV)	40.12475	7,92833	32,53914	21.06673	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
V, (eV)	-20.06238	-3.96416	-16.26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3,45250	-3,45250
E(n m) (eV)	0	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15,35946	-15.35946
ΔΕ <sub>(1,20)</sub> (, o (n) (cV)	0	-0.72457	0	0	0	0	٥	0	0	0	0
Er (20 10) (0V)	0	-13.91032	-15,56407	-15,56407	-14,63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	9865851-
E, (n,in) (aV)	-63.27093	-31,63540	-67,69451	-49.66493	-51.63533	-31.63537	-31.63537	-31.63535	-31,63537	-31.63535	51.63535
$E_T(ahm-alom, nsp^*, AO)$ (eV)	-3.71673	-1.44915	0	. 0	0	-1.85836	-1.85836	-1,44915	-1.85836	-1,44915	-1.44915
E, (10) (0V)	-66.98746	-33.08452	-67,69450.	-49.66493	-31.63537	-33,49373	-33.49373	-33.08452	-33,49373	-33.08452	-33.08452
a (1013 rad 1.5)	19.0113	10.5087	24.9286	24.375!	24.1759	669£+'6	9.43699	15.4846	9.43699	9.55643	9,55643
Er (aV)	12,51354	6.91703	16,40846	15.97831	15,91299	651129	6.21159	10.19220	6.21159	6.29021	12062'9
E, (eV)	-0.25440	-0.17214	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
Ex. (0V)	0.19542	0.10539	0.35532 (Eq. (13.458))	0.35532 (Eq. (13,458))	0.35532 (Eq. (13.458))	1221.0 [2]	0.17978	0.09944	0.12512 [2]	0.12512 [2]	0,12312
E. (aV)	-0.13769	-0.11945	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E (cV)	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
External (eV)	-67.26284	-33.20397	-67.92207	-49.80996	-31.70737	-33.59732	-33.49373	-33.24376	-33.59732	-33.18712	-33.18712
E (4. 10 m) (cV)	-14,63489	-14,63489	-14,63489	-14,63489	-14,63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Emple, so so (cV)	0	0	-13.59844	-13,59844	-13,59844	0	0	0	0	0	0
f: (a) (a,b)	8.72329	3.93419	12.49186	7.83016	3.32601	4.37754	4 7997 I	3 97398	4 17951	3 62178	72.210 E

Table 15.193. The total bond energies of nitroalkanes calculated using the functional group composition and the energies of Table 15.192 compared to the experimental values [3]. The magnetic energy Lag that is subtracted from the weighted sum of the

-																
Ornania.	Name	W	V-7	H.J	H.)	H.)	((a)	(P) (J-)	(c) (c)	C-C (q)	(e) C-C	() ()	4	Calculated	Experimental	Reladire Error
			200											Total Boad	Total Bond	
		Group	ģ											Price (eV)	Energy (cV)	
Γ	Numerhane	-	-	-	0	٥	٥	0	•	c	-	c	0	25.14934	25.107	#0100.0°
	Nitrocthans	~	_	_		٥	_	•	•	O	c	c	0	37.30704	37,272	-0.00040
	I-Nitrochoone	_	_	_	7	c	7	•	•	c	c	0	0	49,46474	49,451	-0.0002x
CHNO	2-Nitropropone	_	_	~	0	_	•	~	•	٥	0	0	0	49.56563	19,602	0.00074
	I-Nitrobutage	_	_	_		۰	_	•	0	٥	0	•	0	41.62244	109.19	-0.00036
	2-Nitroisobatan	-	_	m	0	٥	•		-	c	c	0	7	61.90697	<u>ج</u> ج	0,00061
	1-Nitrocmane	_	_	_	7	٥	-	-	0	0	•	0	0	73.78014	73 7.19	.000028

Almas at Anela	the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the state of the s				t il tangga pina	II ING CAICING	contact where $E_{ij}$ is the caretralion of $\theta_{ij}$ , the parameters from the preceding angle were used. $E_{ij}$ is $E_{ij}$ (atom - atom, and $I_{ij}$ ).	neters from th	he preceding any	gle were use.	d. E, is E,	. (atom - ate	m, msp2, AO						
	7	75.	, 2¢'	E	Atom	L.	Alom 2				,								
	(°	(°°)	Alea (0,)	2 :4	Hybridization Designation	View 5	Hybridization Designation	, al	r į	;	: نی	J.	V'	£ 5	φ, <u>Θ</u>	o- 3	<b>6</b> * 3	0 (J	9. 9.
				-+	(Table 15.3.A)		(Table (5.3.A)							(i)	<u> </u>	Ξ_			=
LNC.H	2#1273	2,04711	3.9663	-14.X2575		-14.55414.	z	121670	0.91140 (Eq. (13.116))	6.73	-	67.0	0.99312	۰	<u> </u>		+	136.17	107 (nitramethans
, OM, O2	2,30843	2.30843	121.7	.11mg/91-	2	-16,68411	7.	0,81349	O.R1549	-	-	-	0.81549	-1.44915	_				<u> </u>
Mathibus ZHC, H	211106	211106	3,4252	-15.75413	-	×	=	0.16359	-	-	-	0.73	1.15796	c				-	107
										T				,			-	¥.	(propane)
ת'נ'נ'															15.00			110.49	(propere) 113.8 (bulanc)
											1						_	_	(technime)
ZC,C,H															1509		-	10.49	(Butane) (111.4
ZHC.H	2,09711	2.09711	3.4252	-15.75493		×	Ξ	0.86339	-	-	-	9.75	1.15706	6	L		+	+-	(sobolare)
ζ,ς,ς,									1	1				,				05,001	
H', ') ') '77											1				70.56		-	109.44	
۳۰ ز." حزر"ز."د	2,915.47	2.91547	4.705K	-16,61412 C.	a	-16,68412	n	O R I SATS	0.81549		-	-	672.16.0		70.56		2		8 9
H'.)')7				-15.55033		-14 12575				1		-		OCEC+11				19.67	(isobotane)
1	73.67	2.11323	4.1633	ڻ'	~	ڻ	_	0.X74US	0.91771	0.75	-	0.75	1.04117	•			=	110.76	
2C,C,H In C,	2.91547	1.00711	4,1633	.13.45033 (°,	3	-14.82373	-	0.X7495	0.91771	82.0	-	57.0	1.04187				=		·
حديدير سردي	2.90327	2.00327	4.705#	.15.55033	3	-14.12375	-	SGP4X D	177160	0.75	-	67.0	19887	ACTIVATION IN					sobstanc)
7C'C'C'						•				1	+						-	<u> </u>	(isobutane)
			j			-	_				•		-			ĺ			

ALKYL NITRITES  $(C_n H_{2n+2-m}(NO_2)_m, n=1,2,3,4,5...\infty)$ 

The alkyl nitrites,  $C_nH_{2n+2-m}(NO_2)_m$ , comprise a RC-O-NO moiety that comprises C-O, O-N, and NO functional groups. The alkyl portion of the alkyl nitrite may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise 5 methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrites are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^22s^22p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  ${}^3P_2$ . The electron configuration of nitrogen is  $1s^22s^22p^3$ , and the orbital arrangement given by Eq. (10.134) has 15 three unpaired electrons corresponding to the ground state  ${}^4S^0_{3/2}$ . The bonding in the nitro (NO) functional group is similar to that in the SO group given previously. It also has similarities to the bonding in the carbonyl functional group. In the NO group, the two unpaired electrons of the O atom form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a double bond. The nitrogen atom is then energy matched to the O-N functional group that is further energy matched to the  $C2sp^3$  HO of the C-O functional group. To meet the equipotential condition of the union of the  $N=O-H_2$ -type-ellipsoidal-MO with other orbitals of the molecule, the hybridization factor  $c_2$  of Eq. (15.51) for the N=O-bond MO given by Eq. (15.140) is  $c_2(O \text{ to } N2p \text{ to } C2sp^3HO) = 0.85987$ .

As in the case of the carbonyl group, two unpaired O electrons result upon bond 25 breakage of the N=O bond which requires that two times  $E_{mog}$  of oxygen (Eq. (15.59)) be subtracted from the total energy of NO. Additionally,  $E_T(atom-atom,msp^3.AO)$  and  $\Delta E_{H,MO}(AO/HO)$  are equal to -0.92918~eV (Eq. (14.513)) which matches the energy of the N=O bond with the contiguous O-N bond and matches the energy contribution of an oxygen atom.

The O-N functional group comprise a single-bond,  $H_2$ -type-ellipsoidal-MO between the remaining unpaired nitrogen electron and an unpaired electron of the second oxygen atom which further forms a single bond with the  $C2sp^3$  HO of the C-O functional group. In alkyl nitrites, the hybridization factor  $c_2$  of Eq. (15.52) for the C-O-bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO\ to\ O)=0.85395$ . The hybridization factor  $c_2$  of Eq. (15.52) for a C-N-bond MO given by Eq. (15.116) is  $c_2(C2sp^3HO\ to\ N)=0.91140$ . Thus, the hybridization factor  $c_2$  of Eq. (15.52) for O-N that bridges the C-O and N=O bonds given by Eq. (15.69) is

$$c_2(N2p \text{ to } O2p) = \frac{c_2(C2sp^3HO \text{ to } N)}{c_2(C2sp^3HO \text{ to } O)} = \frac{0.91140}{0.85395} = 1.06727$$
 (15.141)

10  $E_T(atom-atom,msp^3)AO) = -0.92918 \,eV$  in order to match the energy of the NO group and  $E(AO/HO) = -15.35946 \,eV$  in order to match the C-O functional group.

The C-O functional group is equivalent to that of an ether as given in the corresponding section except that  $E_r(atom-atom,msp^3.AO)$  and  $\Delta E_{H_2MO}(AO/HO)$  are both -0.72457~eV which matches the energy contribution of an independent  $C2sp^3$  HO (Eq. 15 (14.151)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrite.

The symbols of the functional groups of branched-chain alkyl nitrites are given in Table 15.195. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrites are given in Tables 15.196, 15.197, and 15.198, respectively. The total energy of each alkyl nitrite given in Table 15.199 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.198 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrites determined using Eqs. (15.79-15.108) are given in Table 15.200.

Table 15.190	Table 13.196. The peometrical bond parameter		e of alkyl nitrites and experimental values [1]	rimental values [1].								
Parameter	Group	O-N Group	anoso O~J	C~H (CH,) Group	C-H (CH <sub>3</sub> )	C-H Group	Group Group	C~C (b)	C-C (c) Group	C-C (d) Group	C-C (e) Group	C-C
0 (0°)	1.32255	1.76440	1.85327	1.64920	1.67122	1.67465	2.12499	2.12499	2.10725	2,12499	2 10725	2 107
c, (a,)	1.15002	1.32831	1,36135	1.04856	1.05553	1.05661	1,45744	1.45744	1.45164	1.45744	1,45164	1481
Sond 20 (2)	1.21713	1.40582	1,44079	1,10974	E1711.11.	1.11827	. 1.54280	1.54280	1.53635	1.54280	1,53635	1,5363
Exp. Bond Length (A)	1.265 (methyl nitrate) 1.2 (HMC).)	1.402 (methyl nitrate) 1.432	1.437 (methyl nitrate)	1.107 (C - H propane) 1.117	_	1.123 (isobutane)	1.532 (propane) 1.531	1,532 (propane) 1,531	1.532 (propane) 1.531	1,532 (propaue) 1,531	1.532 (propane) 1.531	1.532 (propara 1.531
h.c (a,)	0.65314	1.16134	1,23751	(C-7) Minis	(2012)	1,7007.1	(butane)	(butane)	(butmuc)	(Pulzine)	(butane)	(butan
	0.86955	0.75284	0.73457	0.63580	0.63159	0.63095	009890	0.04870	1.32730	1.34616	1.52750	1.5275
							,,,,,,	255	Cocoo			2000

Table 15.197. The MO to HO intercept geometrical bond parameters of alkyl nithites. R. R. R. me H or alkyl groups. E, is E, (atom - atom, may AO)	netrical bon	d parameters of	alkyl nitrites.	8. N R. nuc H o	or alkyl groups.	Er is Er atom	n – atom, msp′.,	40).							
Bond	Atom	Α,	123	15,4	£,	Final Total	, T	, <u>\$</u>	200	E(C2p")	.8	9	6	9	ď
		(va) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Boud 4	C.2.p.	ર્જે	(°)	Final ()	(eV)	Ξ	©	Ξ	(°)	(%)
RON = O	9	-0,46439	0	•			1.00000	O.NR9N3	-15 20034		137.15	42.83	06'19	0.49764	0.63238
RON = O	2	-D.46459	-0.46459	c	0		0.93084	0.86359	-15.75493		60'YE)	43.91	KP'999	0.52781	177790
RO, - NO,	20	-0.46459	-0.56239	e	0		1,0000	0,86923	15,63263		99,22	NO.7K	47.63	1.18905	0.13925
RO, - NO,	ν	-0,JK459	-0.46459	g	е		0.93014	0.86359	13,73493		98.78	\$1.22	47.30	1.19655	0.13175
RH;C, -0,NO,   R = H,alkyl	0,	•££3£.0-	6Styt Or	. 0	0 -		1.00000	0,86933	.15.63263		91.43	11.57	43.71	1,33962	0 02173
H,C,-0,NO.	]_ C	-0,36229	0	O		151.97798	0,91771	0.89582	-15.17804	-14,99717	17.89	86.29	15.31	130342	0.05793
-CH1H1C, -0,NO,	٠,	4236.0	-0.9291K	0	۰	.152.90716	17710.0	0.64418	-16.11722	-13.92636	19,16	30.EL	42.16	13773	0.01238
$C-H(CH_s)$	, r.	-0,92918	ŋ	ū	0	-152 54487	0.91771	0.86359	-15 75493	15,56407	77,49	15.501	8P'12	1,23564	Q,1870X
( C - H (CH; )		#1050.0-	7 10 20 E	0	0	-153,47406	0,91771	0.81549	-16.68412	-16.49325	68.47	11.5	35,84	135416	0.29933
(C-H (CH)	ü	-0.9291R	-0.9291 K	-0.9291X	e	-154,40324	0,91771	0,77247	-17.61330	-17,42244	61.10	118.90	31.37	1.42988	0,37316
H,C,C,H,CH2,- (C'-C'(a))	(C.	-0.92918	U	c	c	152.54487	0,91771	0,86359	-15.75493	-15,56407	63.82	116.18	30.08	1,53579	0.38106
H,C,C,H,CH, = - (C - C' (B))	ن	-0.9291E	-0 9291R	· c	c	-153,47406	0,91771	0,81549	-16.63412	-16,49325	56,41	65.551	26,06	1.90190	0.45117
$(C-C, \{h, C, H, C, -R\}, HCH_3 - \{C-C, \{b\}\}\}$	ť	-0.92918	-0.9291K	-0.9291x	c	-154.40324	0,9177]	0,77247	-17.61330	-17,42344	48.30	131,70	21.90	1,97162	0.51318
$(R-H_3C_s(R-H_2C_s)C_s(R-H_2C_s)CH_3-(C-C_1C_s)$	ر.	-0,92918	-0.72457	-0.72457	12457	-154.71860	0,9177!	Q.75119	-17.93166	9TT.T.1.	48.21	62.161	21.74	LETZE.1	0.50570
$kaC'.C'.(H_2C, -H')HCH_2 (C'-C'.(d))$	ر د ا	#1676'0-	x1626'0-	к1626.0-	0	-154.40324	0.9177	0,77347	-17.61330	-17.42244	48.30	131.70	21.90	1.97162	0.31388
κτά" (R'-H;C,)C, (R'-H;C,)CH <sub>2</sub> - (C'-C'(Θ))	٠,	-0,724SF	-0.72457	-0.72457	12927.0-	15431379	17710.0	0,76765	-17.92866	-17.75719	50.04	967621	3972	1,94462	0.49292
$urK_s(H_sC_s-R)HCH_s-(C-C_s(G))$	C.	-0,72457	-0,92918	-0.9291k	Ą	-154,19863	12216.0	0,71155	-17,40169	-17.21713	52.78	27.73	24,04	1,97443	0.47279
$kmC_{\mu}(R^{\mu}-H_{\mu}C_{\mu})C_{\mu}(R^{\mu}-H_{\mu}C_{\mu})CH_{\mu}-(C^{\mu}-C^{\mu})CH_{\mu}$	ن	-0.73457	12457 0-	-0,72457	18411.05	6651575}-	12216.0	0.76763	-17.92866	•17.17.11	50.04	56:621	22.66	1.94462	0,49291

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	Group	Group	Group	Group	Group	Oronp	Group	Group	Croup	Group	Croup Group	(E) (J-(J
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(2)	-	-			67.7	6.75	CO	0.5	0.5	ςo	0.5	0.5
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	-	-	-	-	-	-	-	1	-	-	-	-
ړ.	0.85987	1.06727	0.85395	0.91771	0.91771	17710	0.91771	0.91771	177160	0.91771	0.91771	122100
5	2	•	٥	0	_	-	٥	0	c	-		
ζ,	4	2	7	-		-	2	2	, ,	,	-   -	،
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	0.5	0.5	0.5	0.75	37.0	34.0	, ,	, ,	,		0	0
	-	_	-	-	-	-	3	6.3	3	0.5	0.5	0.5
V, (aV)	-108.34117	-42 83043	22 04 173	90465 701.	70.414.05	- 100.00	-	-	-	-	-	-
V (eV)	22.66.103	COSOF OF	2,000	20000	7411-01-	-33.12013	+1767.97-	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
7. (aV.)	40 05030	67.60.40	7,594,50	38.92728	23.78002	12,87680	9,33352	9,33352	9.37273	9.33352	9.37273	9.37273
V (4K)	20,000	12,13739	6.04400	32,33914	21.06675	10,48582	6.77464	6.77464	6.90500	6.77464	6.90500	6,90500
(c) (c)	-20.4 7960	-6.06870	4.31232	-16.26957	-10.53337	-5.24291	-5.58732	-3,38752	-3.45250	-3.38732	-3.45250	-3,45250
(4) (m) (ca )		-15.35946	-14.63489	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	9765E 51-
Oct. n. t. t. v. v. v. (ev.)	-0.92918	0	-0.72457	. 0	•	0	0	0	0	٥	c	
Er (40 10) (eV)	0.92918	-13,35946	-13.01032	-15.56407	-15.56407	-14,63489	-15,56407	-15.56407	9765E 51-	14 56407	14 35046	27031.31
Ky (num) (eV)	-63.27057	-31.63327	-31.63537	-67,69451	-49.66493	-31.63533	-31 63537	71953 IT.	31 6263 6	10,000	0+400-1-	-12,33940
$F_{\tau}(ann - anm, nnp^{*}AO)$ (eV)	-0.92918	-0.92918	-0,72457	٥	6		1 04034	700001	5555010	/tcm:1c-	-31.00333	-31.63535
F. (10) (4V)	-64 19907	23 66455	13 24004	23.05.25		,	1,6000	-1.63630	-1,44915	-1.85836	-1.44915	-1.44915
a (10th rad 1x)	10.710	22.25.00	26.30300	00,00,0	-49,00493	-31.63537	-33.49373	-33.49373	-33.08452	-33,49373	-33.08452	-33.08452
( (aV)	20037	43.3378	20.7301	24.9286	24.2751.	24.1759	9.43699	9.43699	15.4846	9.43699	9.55643	9.55643
F (-1/2)	12.03039	13.37430	13.64490	16.40846	15,97831	15.91299	6.21159	6.21159	10.19220	6.21159	6.29021	6.29021
(7")	0.20387	0.25261	-0.25648	-0.25352	-0.25017	-0.24966	-0.16515	-0.16515	-0.20896	-0.16515	-0.16416	-0.16416
	[46]	[47]	U.13003 [21]	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0.12312	0.17978	0.09944	0.12312	0.12312	0.12312
(cV)	-0.12390	0.19899	-0.16817	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0 10260	0 10050
(; a (eV)	0.11441	0.13441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0 14803	0 14803
f <sub>τ</sub> [νω <sub>σ</sub> ] (σV)	-64.44771	32,76354	-32.52811	-67.92207	-49.80996	-31.70757	-33.59732	-33.49373	-33.24376	-33.59732	-33.18717	C1791 FF.
L'ourse (c. 17 10) (cV)	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14,63489	-14.63489	-14.63489	.14.63489	-14 63489	-14 63480
1. mand 12, 47 may (CV.)	0	٥	0	-13.59844	-13,59844	-13.59844	0	٥	0	0	0	o c
En(ray) (CV)	5.67933	3.49376	3.25833	12.49186	7 22016	.000					,	•

1		T	T	T	T		т-	Т	Т	7-	7		7
Exp. 0	.©		107	107	(propare) (propare) 113.8 (butane) 110.8 (imbutane)	(bulcas) (fl.4 (fccbulcas)				1.10.#		111.4	111.4
Ca. 0	©	113.33	11231	101.44	110,49	110,49	109.50	1700	100 44	110.67	110.76	111.27	111.27
г	, ©							T	T		1		
6	· ©							T	T				
9	Œ				1569	1569		20.56	70.36				
E,	(§.	-1.44915	-1.44915	•			0			-1,85836	G	a	-J #5836
\- 		0.86345	0,81549	1.15796			1.13796			0.81549	1,04887	1,04887	1,041877
٠		-	-	6.75			0,75			-	67.0	67.0	57.0
ບໍ		-	-	-			_			-	-	-	-
ŭ		-	-	-			_			-	57.0	0.75	0.75
ď	Ĩ	0.91140 (Eq. (15.116))	0.81549	-			-			0.R1549	17716.0	17716.0	17716.0
<b>ບ</b> ້	Atom	0,81549	0.81549	0.84339			0.86359			Q.81549	Q.R7495	0,87495	0.87495
Atom 2 Hybridization	Designation (Table (3.3.A)	2	72	x			×			я	-	-	_
Company	Z WON Z	.14,53414 N	110,68411	r			I			-16,68412 C.	.t4.K2373	-14.82373	-14,8233
Alom i Aybridization	Designation (Toble 15.3.4)	æ	\$	,			,			22	~	•	s
f. Carbon	A F	7.) ?!#9'9[*	-16,6 <b>3</b> 411	-15,75493			-15.75493			-16.68412 C' <sub>4</sub>	.13.58037	-15.55033	.15.55m33 (*,
ZC. Terminal	Airm. ( a, )	4.4944	1(13)	3,4252			3,4252			4.795x	₹1633	4.1633	1564.3
ij	<u>9</u>	2.63661	2.65661	2.11106			1.00.2			2.91547	2.11323	1,007[1	2.90327
ZC'	(0,)	2.7270	2.30004	2.11106			2,07711			2,91547	2,91547	2.91547	2.90527
		ע.ס'א	,0N,02	Nebites CHC, H	בנ'נ"נ'	L'C,C'H	CHC, H	7.7.7	Z(',C',H	لاريريز ساري	∠C;C,H ™ C,	ند ري <sup>6</sup> H حزر يو H	سرز" حرر"در"د

ALKYL NITRITES 
$$(C_n H_{2n+2-m} (NO_2)_m, n=1,2,3,4,5...\infty)$$

The alkyl nitrites,  $C_n H_{2n+2-m} (NO_2)_m$ , comprise a RC-O-NO moiety that comprises C-O, O-N, and NO functional groups. The alkyl portion of the alkyl nitrite may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise 5 methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2 CH)$  and t-butyl  $((CH_3)_3 C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrites are equivalent to those in branched-chain alkanes.

The electron configuration of oxygen is  $1s^2 2s^2 2p^4$ , and the orbital arrangement given by Eq. (10.154) has two unpaired electrons corresponding to the ground state  ${}^3P_2$ . The electron configuration of nitrogen is  $1s^2 2s^2 2p^3$ , and the orbital arrangement given by Eq. (10.134) has 15 three unpaired electrons corresponding to the ground state  ${}^4S_{3/2}^0$ . The bonding in the nitro (NO) functional group is similar to that in the SO group given previously. It also has similarities to the bonding in the carbonyl functional group. In the NO group, the two unpaired electrons of the O atom form a MO with two unpaired electrons of the nitrogen atom such that the MO comprises a double bond. The nitrogen atom is then energy matched to the O-N functional 20 group that is further energy matched to the  $C2sp^3$  HO of the C-O functional group. To meet the equipotential condition of the union of the N=O-D functional MO with other orbitals of the molecule, the hybridization factor  $c_2$  of Eq. (15.51) for the N=O-bond MO given by Eq. (15.140) is  $c_2(O to N2p to C2sp^3HO) = 0.85987$ .

As in the case of the carbonyl group, two unpaired O electrons result upon bond 25 breakage of the N=O bond which requires that two times  $E_{mog}$  of oxygen (Eq. (15.59)) be subtracted from the total energy of NO. Additionally,  $E_T(atom-atom,msp^3.AO)$  and  $\Delta E_{H_2MO}(AO/HO)$  are equal to -0.92918~eV (Eq. (14.513)) which matches the energy of the N=O bond with the contiguous O-N bond and matches the energy contribution of an oxygen atom.

The O-N functional group comprise a single-bond,  $H_2$ -type-ellipsoidal-MO between the remaining unpaired nitrogen electron and an unpaired electron of the second oxygen atom which further forms a single bond with the  $C2sp^3$  HO of the C-O functional group. In alkyl nitrites, the hybridization factor  $c_2$  of Eq. (15.52) for the C-O-bond MO given by Eq. (15.114) is  $c_2(C2sp^3HO \ to \ O) = 0.85395$ . The hybridization factor  $c_2$  of Eq. (15.52) for a C-N-bond MO given by Eq. (15.116) is  $c_2(C2sp^3HO \ to \ N) = 0.91140$ . Thus, the hybridization factor  $c_2$  of Eq. (15.52) for O-N that bridges the C-O and N=O bonds given by Eq. (15.69) is

$$c_2(N2p \text{ to } O2p) = \frac{c_2(C2sp^3HO \text{ to } N)}{c_2(C2sp^3HO \text{ to } O)} = \frac{0.91140}{0.85395} = 1.06727$$
 (15.141)

10  $E_T(atom-atom, msp^3.AO) = -0.92918 \ eV$  in order to match the energy of the NO group and  $E(AO/HO) = -15.35946 \ eV$  in order to match the C-O functional group.

The C-O functional group is equivalent to that of an ether as given in the corresponding section except that  $E_T(atom-atom, msp^3.AO)$  and  $\Delta E_{H_2MO}(AO/HO)$  are both  $-0.72457\,eV$  which matches the energy contribution of an independent  $C2sp^3$  HO (Eq. 15 (14.151)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrite.

The symbols of the functional groups of branched-chain alkyl nitrites are given in Table 15.195. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrites are given in Tables 15.196, 15.197, and 15.198, respectively. The total energy of each alkyl nitrite given in Table 15.199 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.198 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrites determined using Eqs. (15.79-15.108) are given in Table 15.200.

lable 15, 195. The symbols of functional groups of alkyl nitries.	THE CHANGE COURS OF MANY CHICAGO.
Functional Group	Group Symbol
NO group	CNN
z.o	N-0
င့	0-0
CH, group	C-H (CH;)
CH, group	$C \sim H'(CH_2)$
₹	H-0
CC bond (n-C)	(8)
CC bond (Iso-C)	(A) L
CC bond (rent-C)	(9) (, -, )
CC (iso to iso-C)	(を) しりし
(24 02)	(e) U)
CC (1 to iso-C)	(S) (1-1)

1 8010 13, 1 VG	able 13.1 yo. 1 he reometrical bond parameters	ond parameters of all	KY INTINCES and exper	mental values [1].		•						
Parameter	OM	N-0	C-0 C-H (CH.)	C-H (CH.)	C-H  CK	(	C-C (a)	C-C (b)	C-C (e)	(P) 2-2	(4) (2)	0-0
	Group	Group	Group	Groun	Group	Group	Group	Group	Group	Group	Group	Group
(0)	1.32255	1.76440	1,85327	1,64920	1,67122	1.67465	2.12499	2.12499	2.10725	1.12499	2.10725	2,10725
(c. (a.)	1.15002	1,32831	1,36135	1.04856	1.05553	1.05661	1,45744	1.45744	1,45164	1.45744	1.45164	1.45164
Bond Length 2c' (A)	1.21713	1,40582	1,44079	1,10974	61711.1	1.11827	1.54280	1.54280	1,53635	1.54280	1.53635	1.53635
Exp. Bond Length (A)	(methyl nimate) 1.2 (HNO.)	(.402 (methy) nitrate) 1.432 (.HXX.)	1.437 (methyf nitrate)	1.107 (C-H propane) 1.117 (C-H butane)	1.107 (C-H propare) 1.117 (C-H butane)	1.122 (isobutane)	1.532 (propane) 1.531	1.532 (propane) 1.531	1,532 (propend) 1,531	1.532 (propane) 1.531	1.532 (propane) 1.531	1.532 (propane) 1.531
1,0 (0,)	0.65314	1,16134	1,25751	1.27293		1.29924	1.54616	(300min)	(501208)	1 54636	(on(ane)	(butane)
J	0.86955	0.75284	0.73457	0.63580	0.63159	0.63095	0.6\$600	0.68600	O 6 RRR	0.68600	0 60969	000070

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Bond	Atom	4.	f.	t'y	E,	Final Total	,1	70,	Eradon	E(C2x0')	.0	9	9	,	
		(cV) Bond 1	(eV) Bond 2	(eV) . Bond 3	(eV) Bond 4	Energy ("2rp"	(°)	(e)	(cV) Final	(eV)	c	· ©	rc	- (°	j (§
RON = 0	9	-0.46459	0	_	ŀ	(cv)	Londo	2 2 2 2 2	16 30034						
ROW = 0	λ	-0.16459	-0 46439	٥	-		7,000	0 0 0 0 0 0	13.4.00		67,15	42.15	67.90	0.49764	Q.63238
RO, - NO,	ď	0.16459	43,572,9	-			1 00000	1,4693	15.659.0		136.139	16.5	66.48	0.52781	0.6221
RO, - NO.	N	-0.46459	-A,46459		0		P40100	0.16140	15 75.102		27.77	× 02	47.63	1.11705	0,13925
RH.CO,NO. R = H.alkyl	70	92235.0-	47,46459	c	٥		1,00000	0.86923	-15.65263		91.43	XR.57	47.30	1.19655	0.13175
H,C,, -0,NO,	ر:	-0,36229	٥	0		X2779.181-	0.91771	0,89582	-15.18104	14.93217	93.71	(X )/4	1537	67.06	2012
-CH,H,C, -O,NO,	٠,٠	-0.36229	N1626 0-	o	0	152,90716	0,91771	0.8441E	-16.11722	15.02636	19.16	¥ 06	42.16	1377	2001718
C - H (CH,)	Ŀ	#16Z6'0"	D	. 0	n	-152.54487	17716.0	0.86359	-15.75493	-15.56407	77.49	15,201	41.48	1,23564	O. 1X 70K
C-H (CH;)	į.	-0.92918	-0 9291K	0	0	-153,47406	17716,0	0.81549	-16,68412	-16.49325	68.47	111.53	J\$.84	135/16	0.29933
C-H (CH)	ن	-0.0291x	-0.92918	N1020.0-	0	-154,40324	0.91771	0.77247	-17,61330	-17,42244	61,10	118.90	31.37	1.42988	0.37326
H,C,C,H,CH, - (C, -C, (a))	٠,	*1020.0-	0	. 40	0	-152,54487	0.91771	0.86359	-15.75493	115.36407	63.82	116,18	30.08	1,85879	0.38106
H,C,C,H,CH;	ť	.0.0291R	816260-	· ·	o	-153,4740%	17716.0	0.81549	-16.68412	.16.49325	56.41	123.59	26,06	1,90,990	0,45117
R-H;C,C,(H;C,-H)HCH;-	ť	40,92918	-0.92918	.0.92918		-154.40324	17716.0	0,77247	-17,61330	ALCTA, Ci-	41,30	131.70	21.50	501761	KALISO
$R - H_1C_*(R^- + H_2C_*)C_*(R^- + H_2C_*)CH_1 - (C^ C^-)$	ن	.0.9291R	-0.72457	-0,72457	.0.72457	-154,71860	0.91771	0.73889	-17.92866	0.73771.	48.21	131.79	21.74	A5726.1	0.50570
(C, -C; (A); (A); (A); (A); (A); (A); (A); (A)	ť	-0.923fk	#16Z6'U*	-0.9291К	-	-154,40324	17716.0	0.77247	-17.61330	17,42244	48.30	131.70	21.90	1,97162	NEISO
(C-C, C) $(C-C, C)$	ن	-0.72457	-0.72457 .	-0.72457	-0.72457	-154,51399	17710.0	0,76765	-17.92kG6	ett.7.7.1.	\$0.04	129.96	22.66	1,944/12	0.49258
$\iota \iota \sigma \iota \iota' \iota \iota' \iota' (H_i \iota' \iota - R^i) H \iota H_i - (\Gamma - \Gamma \cdot (D))$	ر:	-0.72457	11626'0-	-0,929FR	٥	-154,19863	17716.0	0.78155	-17.40809	-17.21783	32.78	12721	24.04	1,92443	0.47279
$BoC_{a}(R-H_{2}C_{3})C_{b}(R-H_{3}C_{3})CH_{3} (C-C_{3}C_{3})$	:	-0.72457	-0.72457	-0.72457	-0.72457	.154.51379	17710.0	0.7676.5	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.47Z9R

	Group	N−0 Group	O-O Group	ć.*,	* E	C-H Group	C-C (a)	C-C (b) Group	C-C (c) Group	C-C (d) Group	ر-ر (e) Group	() Croup Group
n,	7	-	-	9	2	-	-	-	-	-		_
n,	0	0	0	2	-	0	0	0	0			
n,	C	0	٥	٥	0	٥	0	0	o	0	0	٥
ر:	0.5	0.5	5.0	0.75	0.75	0.75	0.5	0.5	6.5	0.5	0.5	29
	1	1	-	-	_	-	-			-	-	-
c,	1	- 1	-	-		-	_	-	-	-	-	-
5*	0.85987	1.06727	0.85395	17716.0	17416.0	17710	0.91771	0.91771	0,91771	0,91771	17716.0	17716.0
ر.	2	0	0	0	-	-	0	۰	٥	-	1	
c,	4	2	2		-	-	2	2	2	2	2	2
ů,	0	0	Đ	3	2	-	0	0	0	٥	0	0
	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	0.5
	1	-	-	-	1	-	_	-	-	-	-	1
V, (cV)	-108.34117	-42.83043	-32.04173	-107.32728	-70.41425	-33,12015	-28.79214	-28.79214	-29,10112	-28.79214	-29.10112	-29.10112
V, (eV)	23.66182	20.48593	9,99436	38.92728	23.78002	12.87680	9,33352	9,33352	9,57273	9.33352	9,37273	9.37273
r (eV)	40,95920	12.13759	8.64465	32,53914	21.06675	10.48582	6,77464	6.77464	6.90500	6.77464	6.90500	6.90500
V, (eV)	-20.47960	-6.06870	4.32232	-16.26957	-10,53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	-3.45250
E(w m) (eV)	٥	-15.35946	-14,63489	-15.56407	-15.56407	-14.63489	-15.56407	-15,56407	-15.35946	-15.56407	-15,35946	-15,35946
OF a, we lan not (oV)	-0.92918	0	-0.72457	. 0	0	0	0	0	0	0	0	0
Er (20 m) (eV)	0.92918	-15.35946	-13,91032	-15.56407	-15,56407	-14.63489	-15.56407	-15.56407	-15,35946	-15.56407	-15.35946	-15.35946
F. (u, m) (cV)	-63.27057	-31.63527	-31,63537	-67.69451	-40,66493	-31.63533	-31.63537	-31.63537	-31.63535	-31,63537	-31.63535	-31,63535
F. (atom - atom, asp', AO) (eV)	-0.92918	-0.92918	-0.72457		0	0	-1.85836	-1.85836	-1,44915	-1.85836	-1.44915	-1.44915
F, (10) (eV)	-64.19992	-32.86485	-32.35004	-67.69450	-49,66493	-31.63537	-33,49373	-33.49373	-33.08452	-33,49373	-33.08452	-33.08452
w (10" rad 1s)	19,2199	23,3578	20.7301	24.9286 ·	1872.42	24.1759	9.43699	9,43699	15.4846	9.43699	9.55643	9.55643
Fr (eV)	12.65039	15.37450	13.64490	16.40846	15,97831	15.91299	621159	6.21159	10.19220	6.21159	6.29021	6.29021
En (uV)	-0.22587	0.25261	-0.23648	-0.25352	-0.25017	-0.24%6	-0.16515	-0.16515	-0.20896	-0.16315	-0.16416	-0.16416
F. (aV)	0.203%	0.10725	0,13663	0.35532 (Eq. (13.458))	0.55532 (Eq. (13.458))	0.35532 (Fa. (13.458))	0.12312	0.17978	0.09944	0,12312	0.12312	0.12312
E., (eV)	-0.12390	0.19899	-0.16817	-0.22757	-0.14502	-0.07200	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	-0.10260
E. (aV)	0.11441	0.11441	0.14803	0,14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_T(r_{ang})$ (cV)	-64.44771	32,76354	-32.52811	-67.92207	-49,80996	-31.70737	-33.59732	-53,49373	-33.24376	-33,59732	-33.18712	-33,18712
E meny (s. 10 111) (eV)	-14.63489	-14,63489	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Freed by so my (aV)	0	0	0	-13.59844	-13.59844	-13.59844	0	0	0	0	0	0
(1.7.7.7.2)												

(J) 2-2 (;-C (e)

Table 15.199. The total band energies of alkyl nitries calculated using the functional group composition and the gnergies of Table 15.199 compared to the experimental values [3].

Formula None None NO C-N C-O CH, CH, CH, CH, C-C (a) C-C (b) C-C (c) C-C (d)

Group Group Group

			_	_	,									
	Exp. θ (e)		1.017	107 (propane)	112 (propane) 113.8 (batane) 110.8	(butand)	(scopmane)			1.1Q.R (isobulane)		(Gobburge)	(111.4	
	Cal. 6	13,33	112.38	101.44	110.49	110.49	109,50	100.44	100.44	110,67	110.76	1113	111.27	
														T
	o. O					_								T
	ø, 💽				15.09	15.60		70.56	70.56					5
	E <sub>7</sub> (eV)	-1.44915	-1.44915	0			c			-1,85836	0	0	-1.R\$R36	
tom, msp' AO).	\$	D,26345	0.81549	1.15796			1.15796			6F\$18'0	1,04887	1,04887	1,04897	
E <sub>r</sub> (atom – a	· ·		-	a.75			0.75			-	6.75	0.75	57.0	
cd. E, is I	<u>ن</u>	-	-	-			-			-	-	-	-	
ngle were us	υ	_	-	-			_			-	0.75	6.75	0.75	
e preceding a	C <sub>2</sub>	0.91340 (Eq. (15.116))	0.81549				-			0,81549	17710	17116.0	0,91771	
meters from th	S Alen I	0.81549	0.81549	0.86359			0.86359			0.81549	0.17495	0 17495	0,17405	
tion of $\theta$ , the para	Atom 2 Hytridization Designation (Table 13.3 A)	×	75	π			Ξ			ม	-		_	
n the calcula	Contract Annual 2	-1453414 N	-16,61411 O	Ŧ			π			-16,68412 C.	-14.82575	-14.82575 C.	-11.17.23.73 C.	
ental values [1].	Atom I Hybridization Designation (Table 13.3.A)	15	p2 .	7			٠,			n	f		\$	
and experin	E E	-16.68417 C.	16,68411	-15.75493			-15,75493			-16.6KH12	.15,55033	1.5 SS033	-15.58053	
slkyl nitrites	2c' Tembul Abrew (G <sub>b</sub> )	4,4944	4,1331	3,4252			3.4252			4.795K	4.1633	4 1633	4,7958	
ameters of a	2c' Bond ) (O <sub>6</sub> )	1.68661	2.63661	3.11106			1.00711			2.98547	2.11323	2.09711	2.90327	
nd angle par	. 2¢' Dmd I (o <sub>0</sub> )	2.727.0	2.30004	2,11106			2,09711			2.91547	291347	2+5167	2,90327	
Table 15.200. The band angle parameters of alkyl nitries and experimental values [1]. In the calculation of 0, the parameters from the preceding angle were used. E, is E, (anni - oron, nay AO)	· Assert of Ataba	אכס'א	40,NO,	H"JH7	תנ"נינ"	H'.5'.H	CHC H	, '.'.'.' 70, '.'.'	H'.J".J7	ייי כ" קנ"נ"נ"	ZC,C,H № C.	וייז נג" "לג"ל," א	אינו נ" קנ"נ"ל."	'5'.5'.57

ALKYL NITRATES  $(C_n H_{2n+2-n} (NO_2)_m, n = 1, 2, 3, 4, 5...\infty)$ 

The alkyl nitrates,  $C_n H_{2n+2-m}(NO_3)_m$ , comprise a  $RC-O-NO_2$  moiety that comprises C-O, O-N, and  $NO_2$  functional groups. The alkyl portion of the alkyl nitrate may comprise at least two terminal methyl groups  $(CH_3)$  at each end of the chain, and may comprise methylene  $(CH_2)$ , and methylyne (CH) functional groups as well as C bound by carbon-carbon single bonds. The methyl and methylene functional groups are equivalent to those of straight-chain alkanes. Six types of C-C bonds can be identified. The n-alkane C-C bond is the same as that of straight-chain alkanes. In addition, the C-C bonds within isopropyl  $((CH_3)_2CH)$  and t-butyl  $((CH_3)_3C)$  groups and the isopropyl to isopropyl, isopropyl to t-butyl, and t-butyl to t-butyl C-C bonds comprise functional groups. The branched-chain-alkane groups in alkyl nitrates are equivalent to those in branched-chain alkanes.

The  $NO_2$  functional group is equivalent to that of nitro alkanes with the exception that  $\Delta E_{H_2MO}(AO/HO)$  as well as  $E_T(atom-atom,msp^3.AO)$  is equal to -3.71673 eV in order to 15 match the group energy to that of the contiguous O-N bond. Furthermore, the O-N group with  $E_T(atom-atom,msp^3.AO) = -0.92918 \, eV$  is equivalent to that of nitrites as given in the corresponding section.

The C-O functional group is equivalent to that of an ether as given in the corresponding section except that  $E_T(atom-atom,msp^3.AO)$  and  $\Delta E_{H_1MO}(AO/HO)$  are both 20 -0.92918 eV which matches the energy contribution of an independent  $C2sp^3$  HO (Eq. (14.513)). Also, the energy terms corresponding to the oscillation of the bond in the transition state are matched to a nitrate.

The symbols of the functional groups of branched-chain alkyl nitrates are given in Table 15.201. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and 25 energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of alkyl nitrates are given in Tables 15.202, 15.203, and 15.204, respectively. The total energy of each alkyl nitrate given in Table 15.205 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.204 corresponding to functional-group composition of the molecule. The bond angle parameters of alkyl nitrates determined using Eqs. (15.79-15.108) are given in Table 15.206.

Harmonia (H. 1980), a reconstruction

	(J-)	Group		2.10725	1 46164	1.45164	30763 1	CCOCC		1.532	(Dronane)	331	(Autono)	(alleria)	1 57750	20.47.
	(e) 2-2	Group		2.10725	1 45164	315	359151			1,532	(propane)	1.531	(butane)		1.52750	
	(p) 2~2	Cimoup		2.12499	1.45744		1.54280			1.532	(propane)	1.531	(butane)		1.54616	
	(a) 2 - 3	dnoso	2 10000	4,10725	1.45164		1,53635			1.532	(propane)	155.	(butane)		05/751	
	(Q) (C)	400	7 12/00		1.45744		1.54280		1	760)	(propane)	160	(onizine)	1 57516	0101-011	
	Groun		2 12499		1.45744		1.54280		.51	(arrano)	153	100	(Dinaine)	1 54616	210.00	00,000
l	Group		1.67465		1.05661		1,11827				(isobutane)			1.29924		2007
1	$(H_1)^{H_1}$	Group 1,67122		. 0666-	(,0333)		1.11713		. 1.107	(C - H propane)	1.117	(C-H butane)		1.29569	27.67.0	7
(0.00) 11 .0.	$(u_1)$		1.64920	1.04856	00000		1.10974		1.107	(C-H propane)	1.117	(C H butane)	20000	1.27293	083590	20.00
020	Cionb	10000	1.83991	1.35643.			1.43559	-		1.437	(methyl nitrate)		1 24213	7	0.73773	
N-0	Group	1 76440	Other 1.	1.32831			1.40582	, 400	(medbar)	(meany) mirrate)	Contra	( TIME)	PE 191 1		0.75284	
wo,	Group	1 29578		1.13815			1.20456	1 205	(methyl nitrate)	12	CHNO	111111111111111111111111111111111111111	0.61857	27,000	0.87862	
20011000		a (a)		(°)	Bond	Lenuth	2c' (A)	200	CAD. Dong	Cengra	₹		h,c (a,)		١	

Bond	Атош	44	£,	F <sub>T</sub>	Εţ	Final Total	7	[3	Erastan.	$E(C2sp^2)$	.0	6	9	q	d'
		(eV) Bond 1	(eV) Bond 2	(cV) Bond 3	(eV) Bond 4	(2 / 2 / 2 / 2 / 2 / 2 / 2 / 2 / 2 / 2 /		(°)	(SV)	Final (	E	©	©	(*)	(°)
RN(O) = O	2	×1626.0	٥		ė		00000 1	0.86359	15.73493		13x 49	41.51	02.29	271670	0 (467)
RN(O) = O	2	A1050.0-	41.92918	USPST'U-	G.		0,93024	0.7/340	.17.14K70		135.60	4.6	63.83	657(33	0.56682
RO, -N(O.),	ď	68PJP'0-	4146459	U			1.00000	0,86359	.(5.75493		94.78	11.22	47.30	1.19635	0.13175
RO, -N(O,),	N	-0.46459	4,92913	-0.9291K.	-		0,93014	0.79340	-17,14870		92.78	17.22	43.03	1,2KD78	0,03852
$RH_1C_1 - O_1N(O_2)_1$ $R = H, alk_3 V$	*0	· 05+9+'0-	-0.46459		6		1,0000	0.86359	-15.75493		27.13	\$7.87	43.9%	132431	0.63212
$H,C_{\omega} = O_{\omega}N(O_{\omega}),$	ر:	-0.46459	0	c	•	-152,0R02R	17719,0	D.KRUN3	- is.20034	-15.00948	95.42	15.64	\$55	(7887)	17770,0
-CH, H, C, -O, N (O,),	ئ	-0.46459	-0.0291R	0	0	-153,00946	0,91771	0.85885	-16.21952	-16,02856	19.90	90.10	47.44	1.35787	0.00143
< H (CH,)	Ü	-0.9291K	. 0	C	0	.152.SAMR7	17116.0	0.86339	-15.75493	-15.56407	77,43	102.51	41,48	123561	Q. IKTOR
('-H (CH;)	Ü	-0.92918	4,92918	. 0	0	-153,47406	0.91771	0.81549	-16.68412	-16,49323	68.47	111.53	35.84	1.35486	0.29933
('-H (CH)	ij	-0,9291#	41,92918	.0.92918	0	-154,40324	0,91771	172277.0	.17.41330	-17,42244	61,10	118.90	31,37	1.42988	0.37326
H,C,C,H,CH, (C'-('(0))	Ü	R1020.0-	0	ø	0	-152 Sealt7	0.91771	0.86359	.15.75403	-13,56,407	63.82	116.18	30,0%	1,83879	0.38106
H <sub>1</sub> C,C,H <sub>2</sub> CH <sub>2</sub> - (CC (a))	1)	41026.0-	#1676U-	0	0	-153,47406	17716.0	0.81549	-(6 68412	-16,49325	36.41	12.59	36.06	1,90850	0,45117
$R = H_s C_s (H_s C_s - R^s) H C H_s - (C - C^s(b))$	•,)	-0.9291R	419291K	ж1626.0-	0	-154,4Q724	0.91771	0.77247	-17,61330	-17.42244	48.30	131.70	21.90	1,57162	0.51348
R-H.C.(R-H.C.)C.(R-H.C.)CH; - (C-C.(c))	5.5	ж) 6 <u>7</u> 929 (ж	40,72457	-0.72457	-0.72437	-154.71860	0,91771	0.75889	-17.92866	67.67.71-	41.21	61.10	21.74	H2861	0.30570
$LoC_{\mathcal{C}_{*}}(H_{\mathcal{L}_{*}}-R^{*})HCH_{\mathcal{L}_{*}}-$ (('-(' (d))	1.)	xiczgo-	x1676Tr	N10270.0-	9	-154,41324	0.91771	0.77247	.17.61330	PACO.71.	48.30	131.70	21.90	1,97162	0.51388
$ler(C_{i}(R-H_{i}C_{j})C_{i}(R^{n}-H_{j}C_{i})CH_{j}-C_{i}(R^{n}-H_{j}C_{i})CH_{j}$	٠,٠	-0.72437	-0.72457 .	-0.72457	-0.72457	.154,51399	0,91771	0.76763	-17.92866	-(7.73779	\$0.04	120.96	22.66	1.5462	0.49298
$w(K', C', (H, C', -K') H C H_2 - (C) = (C)$	".	-0.72457	ж16°С О-	81626.0.	占	.154.19863	0,91771	0.78155	-17.40869	-17,21783	87.78	17.73	24.04	1,924G	0.47279
$kmC_{\mu}(R-H_{3}C_{\mu})C_{\mu}(R-H_{3}C_{\mu})CH_{2}-C_{\mu}C_{\mu}C_{\mu}C_{\mu}$	C.	-0.72457	-0.77457	-0.72457	-0.72457	.154.51399	0.91771	0.76763	-17.92866	-17.73779	50.04	129.96	22.66	1.94462	0.49298

Table 15.203. The MO to HO intercept geometrical bond parameters of alkyl airmies. R.R., R" are H or alkyl groups. E, is E, (anim - ataa, any 'AO).

Bond

ratalingicas	Group	O-N	Granb Quanb	C.H.	£ 2	Selle Galle	C-C (a)	Group Group	(c) (c) (d) (d)	C-C (3)	(e) U-U	ر-د ( <del>)</del>
n,	1	-	-	7	2	-	_		-	-	-	-
	0	0	0	2	-	0 .	۰	0	0		. 6	
n,	٥	0	0	0	0	0	٥	0	0	0	c	6
	6.0	. 0.5	6.0	0.75	0.75	0.75	0.5	0.5	0.5	0.5	0.5	2
	,~	-	1	-	-	-	_	-	-	-	_	-
· ·	-	1	-	-		-	-	-	_	-	_	-
٠	0.85987	1,06727	0.85395	0,91771	17710.0	17719.0	17716.0	0.91771	17710	17710	177160	12190
63	0	0	0	0	_	-	0	0	0	-	_	
6,	4	2	2	1	1	-	2	7	2	2	2	7
6,	٥	0	0	3	2	-	٥	0	0	٥	0	0
	0.5	0.5	0.5	0.75	0.75	0.75	0.5	0.5	0.3	0.5	0.5	0.5
	-	-	_	-	~	-	1	-	-	-	_	-
V, (eV)	-(12,63415	-42.83043	-32,35681	-107,32728	-70,41425	-35.12015	-28.79214	-28.79214	-29.10112	-28.79214	-29.10112	-29.10112
V, (c.V.)	23.90868	20,48593	10.03058	38.92728	25.78002	12.87680	23225.0	9,33352	9.37273	9.33582	9.37273	9.37273
(av)	43.47534	12.13739	8.79304	32,53914	21.06675	10.48582	6.77464	6.77464	6.90500	6.77464	6.90500	6.90500
(eV)	-21.73767	-6.06870	-4.39652	-16,26957	-10.53337	-5.24291	-3.38732	-3.38732	-3.45250	-3.38732	-3.45250	3,45250
El. o 10) (cV)	. 6	-15,35946	-14.63489	-15.56407	-15.56407	-14.63489	.15,36407	-15.56407	-15.35946	-15,56407	-15.35946	-15,35946
D'injan ( w) noi (cV )	-3.71673	٥	-0.92918	٥	٥		0	0	0	o	0	0
$E_r(x_1, x_2)(cV)$	3.71673	-15.35946	-13.70571	-15.56407	-15.56407	-14.63489	-15.56407	-15.56407	-15.35946	-15.56407	-15.35946	-15,35946
F. [11, 110] (cV)	-63.27107	-31,63527	-31.63542	-67.69451	-49,66493	-31.63533	-31,63537	-31,65537	-31,63535	-31,63537	-31.63535	-31.63535
Er (arom - atom, nap".AO) (cV)	-3.71673	-0.92918	-0.92918	0	0	0	-1.85836	-1,85836	-1.44915	-1.85836	-1.44915	-1.44915
E, (un) (cV)	-66.98746	-32,56455	-32.56455	-67.69450	-49,66493	-31.63537	-33,49373	-33.49373	-33.08452	-33.49373	-33.08452	-33.08452
a (10° rad/s)	19.8278	23.3578	21,0910	24,9286	24,2751	24.1759	9.43699	9.43699	15.4846	9,43699	9.55643	9.55643
E <sub>1</sub> (aV)	13.03099	15.37450	13.88249	16.40846	15.97831	15.91299	6.21159	621129	10.19220	621159	6.29021	6.29021
F. (6V)	-0.23938	0.25261	-0.24004	-0.25352	-0.25017	-0.24966	-0.16515	-0.16513	-0.20896	-0.16515	-0.16416	-0.16416
f. <sub>tru</sub> (dV)	(45)	0.10725	0.15663	0.35532 (Eq. (13.458))	0.35532 (Eq. (13.458))	0,35532 (Eq. (13,458))	0.12312 [2]	0.17978	0.09944	0.12312	0.12312	0.12312
£_ (aV)	-0.14267	0.19899	-0.17172	-0.22757	-0.14502	-0.07700	-0.10359	-0.07526	-0.15924	-0.10359	-0.10260	0,10260
E (cV)	0.11441	0.11441	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0,14803	0.14803
F. ( may ( a) V )	-67.27281	32.76354	-52.73627	-67.92207	-49.80996	-31,70737	-33.59732	-33,49573	-33.24376	-33.59732	-33.18712	-33.18712
the war lay set Try (CV)	14,63480	-14.63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
E (4, 10 10) (cV)	0	0	0	-13.59844	-13.59844	-13.59844	o	0	e	0	0	
E,, khurn (c/)	8.73325	3,49376	3.46649	12.49186	7.83016	3.32601	4.32754	4.29921	3.97398	4 17011	3,67128	1 01 724

Table 15.205. The total bond energies of alkyl nirrates calculated uping the functional group composition and the energies of Table 15.204 con Formal Name of the second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second second s

Relaire Error	0,00244 0,00131 0,00095 0,00213
Experimental Total Bond	Enery (eV) 28.117 40.396 52.550 52.725
Culculated Total Bond	Enery: (eV) 18.1836 40.34366 51.50076 52.60165
0) 2-2	0000
(e) 2-2	0000
(p) 2-2	8000
C-C (c)	2000
(p)	0001
CH C-C (a)	ė-~o
#J	00
Ĕ,	0 - 10
ť.	
C-0 Group	
O-N Group	
Group	
Name	Methyl nitrate Ethyl nitrate Propyl nitrate Copropyl nitrate

_		_		_		_	·	_		_				,	_				· -	_
Exp. 9	Œ			110 (method mitmer)	103 (mathyl nileate)		(methyd mitrate)	112.4 (methyl nitrate)	(methyt nitrats)	107 (prepare)	(propare) (propare) 113.8 (butane) 110.8 (sasbutane)	11[.0 (buram:) 11[.4 (isobutane)				110.R (Isobutane)		111.4 (isobutane)	. 111.4 (szobadzaz)	
Cal. 0	ε		05.601	100,44	10001	129.83	115.09 (Ea (15.99))	(Eq. (15.99))	112.79	108.44	110.49	110.49	100.50	109.44	102.44	29011	110.76	111.27	111.27	107.50
6	Œ																			
6	· ©						129,83	129,83												Γ
6	. ©			70.56							15031	15.69		70.56	70.56					02.57
. I	(§		0			-1.44915			-1,44915				•			-1.85836			-1,85836	
c. diam.msp .A	r		1,15796		2501670	0,81549			0.16345	1,15796			1,15796			0.81549	1.04887	1,04117	1.04KK7	
Cr arom	,		0.75		A73	-				67.0			0.75			7	67.0	0.75	0,75	
2 2			_		-	-			-	-			-			-	-		-	
C. C.			-		67.0	-			-	-			_			-	Q.73	0,75	0.75	
tu me breceung	Arra 3		· <b>-</b>		0,15395 (Eq. (15.114))	0,81549			0.91140 (Eq. (15.116))	-			-			0.81549	12/1/1	17710.0	0,91771	
c,	, i		0.86359		1221610	0,81549			0.81549	0.46359			0.KG359			0,81549	0,K7493	0,X74735	0,87495	
Atom 2	Hybridization Designation	(Table 13.3.A)	'n		0	2			z	x	·		± .			. 25	_	-	-	
	ĵ		. <b>.</b>		-13.61806	-16.68411°		i	-[4.534]4 N	π	<del></del>		ı			. 16,68412 (',	-14.82575 . (' <sub>A</sub>	-14.R2573 (°,	-14.K2575	
Alom I	Hybridization Designation	(Table 15.3.A)		4	-	*			ุล	,			,			57	~	٠ ،	\$	
E	) s u	) may	-15.75493		-14.W2575	-16.68411 O			.15.61412 (',	-15.75403		_	-15.75493			-10 6K412	-15 55033 C.,	-15.55033	-15.35033	
2c		\mathbb{B}	34252		3.723K	4.1231			122979	2527-12			3.4252			4.795K	4.1633	4.1633	4 7058	
25.	Ĩŝ		2.09711		2,71287	2,27630			2.65661	2.11116			200711			2.91547	αξιιτ	2.09711	2,903,27	
20,	Īŝ		1117201.5		1,100,11	2,27630			2.71217	2.11106			2.09711			1.91547	1.91547	19197	1.9037	
Annual Jacob and angle parameters on any minates and experimental values [1]. In the calculation of the parameters and the parameters are seen and the parameters and the parameters and the parameters are seen and the parameters and the parameters are seen and the parameters and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the parameters are seen and the			ZHC.H	'0'.5'H7	'0''''7H7	, CO , NO.	CO NO	ON"07	<i>ห</i> ืบJ7	H". JH7	7C.S.S.	H'.5".17	H.JHZ		H".",77	ب. ر. ۳۰ د. د.	") == H".3".17	#.J.H 	سار* حرير*ر* .	<i>'.j".j",</i>

#### CYCLIC AND CONJUGATED ALKENES

$$(C_n H_{2n+2-2m-2c}, n=3,4,5...\infty, m=1,2,3..., c=0 \text{ or } 1)$$

The cyclic and conjugated alkenes are represented by the general formula  $C_nH_{2n+2-2m-2c}$ ,  $n=3,4,5...\infty$ , m=1,2,3..., c=0 or 1 where m is the number of double bonds 5 and c=0 for a straight-chain alkene and c=1 for a cyclic alkene. They have at least one carbon-carbon double bond comprising a functional group that is solved equivalently to the double bond of ethylene. Consider the cyclic and conjugated alkenes 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-cyclopentadiene, and cyclopentene. Based on the condition of energy matching of the orbital, any magnetic energy due to unpaired electrons in the constituent 10 fragments, and differences in oscillation in the transition state, five distinct C-C functional groups can be identified as given in Table 15.208. The designation of the structure of the groups are shown in Figures 61A-E. In addition,  $CH_2$  of any  $-C=CH_2$  moiety is an conjugated alkene functional group. The alkyl portion of the cyclic or conjugated alkene may comprise at least one terminal methyl group  $(CH_3)$ , and may comprise methylene  $(CH_2)$ , and methylyne 15 (CH) functional groups that are equivalent to those of branched-chain alkanes.

The solution of the functional groups comprises the hybridization of the 2s and 2p AOs of each C to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. The C-C groups are solved in the same manner as those of the 20 branched-chain alkanes given in the corresponding section. For example, the cyclopentene  $C_a - C_b$  group is equivalent to the n-C-C alkane group. Many of the corresponding energies of the molecules of this class are similar, and they can be related to one another based on the structure. For example, cyclopentadiene is formed by ring closure of 1,3-pentadiene with the elimination of H from the terminal methyl and methylene groups. Thus, the energy of each of the corresponding carbon-carbon bonds in cyclopentadiene is the same as that in 1,3-pentadiene except that the difference between the energies of the 1,3-pentadiene  $C_c - C_d$  and the cyclopentadiene  $C_a - C_b$  groups is the magnetic energy (Eq. (15.58)) which is subtracted from the  $C_a - C_b$  total bond energy according to Eqs. (13.524-13.527) due to the formation of a CH group from the methylene group.

 $E_T(atom-atom, msp^3.AO)$  of the C=C-bond MO in Eq. (15.52) due to the charge donation from the C atoms to the MO is equivalent to that of ethylene,  $-2.26759 \, eV$ , given by

Eq. (14.247).  $E_r(atom-atom, msp^3.AO)$  of each C-C-bond MO in Eq. (15.52) is -2.26759~eV or -1.85836~eV based on the energy match between the  $C2sp^3$  HOs corresponding to the energy contributions equivalent to those of alkene, -1.13379~eV (Eq. (14.247)), or methylene, -0.92918~eV (Eq. (14.513)), groups, respectively, that are contiguous with the C-C-bond carbons. In the former case, the total energy of the C-C bond MO is matched to that of the alkane energy in the determination of the bond length. The charge density of 0.5e must be donated to the C-C bond in order to match the energy of the adjacent flanking double bonds. This further lowers the total energy of the C-C-bond MO and increases the C-C bond energy. This additional lowering of the C-C-bond energy by additional charge donation over that of an alkane bond due to adjacent double bonds is called *conjugation*.

The symbols of the functional groups of cyclic and conjugated alkenes are given in Table 15.207. The structures of 1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, 1,3-cyclopentadiene, and cyclopentene are shown in Figures 61A-E, respectively. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) 15 parameters of cyclic and conjugated alkenes are given in Tables 15.208, 15.209, and 15.210, respectively. The total energy of each cyclic or conjugated alkenes given in Table 15.211 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.210 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum 20 of the  $E_D(Group)$  (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of cyclic and conjugated alkenes determined using Eqs. (15.79-15:108) are given in Table 15.212.

Table 15.207. The symbols of functional proups of cyclic and conjugated alkenes.	ups of cyclic and conjugated alkenes.
Functional Group	Group Symbol
CC double bond	رڍي
1,3-butodiene, 1,3-pentadiene CC.	
1,3-cyclopentadiene (', - (',	(r) )-
1,3-pentadiene (;, -(',	2 4 4
cyclopentene (',(',	(6) ]- ]
.4-pentadiene (', - (',	() -(, (c)
"3-cyclopentadiene C., - C.,	(, -(, (q)
syclopentens ( ( ,	(()
CH <sub>2</sub> alkenyl group	$C = H\left(cH_2\right) \oplus$
CH, group	C-H (CH,)
CH; alkyl group	$C - H\left(CH_{3}\right)$ (ii)
HO	r-H

00290	0.63159	0.63580	0.63756	0.68600	0.69887	0.69887	0,69887	0.72309	0.86030	ъ
1.2992	1.29569	1.27295	1.26354	1.54615	1.46439	1.46439	1,46439	1,32110	0.75055	h,c (a,)
i. 124 (isobuta	(C - H butune)	(C-H butane)	1.108 (avg.) (1.3-buadenc)	(eyclopentene)	(1,3-eyclopentadiene)		(cyclopentene)	1,469 (1,3-cyclopentadiene)	(1,3-cyclopentadiene) 1,342 (cyclopentene)	3
1.12		1.107 (C - H properte)	1	1.546	1.509		915.1	1.467 (1,3-butadiene)	1.349 (1.3-butadiene) 1.342	Exp. Bond Length
1.1182	1.11713	1.10974	1,10668	1.54280	1.51437	1.5 1437	1.51437	1,46365	1.34052	Bond Length 2c' (A)
1.0566	1.05553	1.04856	1.04566	1,45773	1,43087	1.43087	1,43087	1.38295	1,26661	c, [a]
1.6746	1.67122	1,64920	1.64010	2.12499	2.04740	2.04740	2.04740	1.91256	1.47228	o (a,
Grou	(ii) Group	Group	(i) Group	Group	Group	Огоир	Grøup	Group	Group	
1.5	(40) 11-0	(-H (CH.)	C-# (CH.)	رر (e)	ن-ر. (q)	(. – (. (e)	(a) .),	(:) (:)	0	Parameter

	Atom	5 <sub>7</sub> (eV) Bond ا	f.r (eV) Band 2	E <sub>7</sub> (eV) Bond 3	F <sub>T</sub> (eV) Bond 4	Final Total Energy (.2sp* (eV)	<u>(e)</u>	(°)	Enan (C147) (eV) Final	E(C2sp²) (eV) Final	.) (•)	, (°)	, (°)	(a,)	(a,)
$H_1C_s = C_s(H)(H)C = CR$ (1.3-butadium, 1.3-pentadiene) $H_1C_s = C_s(H)C_sH_2C_s(H) = C_sH_1$ (1.4-pentadiene)		-1.133кв	С	e .	в	-152.74JAD	177100	0.85252	-13.9395	-15.758KB	129.RH	50.16	60.70	0.77040	0.54620
$H_1C_n = C_n(H)(H)C_n = CR$ (1.3-butadiens, 1.3-peniadiene) $-HC_n = C_n(H)(H)C_n = C_nH -$ (1.3-cyclopeniadiene)	3 0	-1.133кр	-1, f.D.kn	e	<b>a</b>	#ZDarES1-	17718.0	70267.0	-17,00334	81C0C91-	27.13	32,87	t.r.	0.78613	0.48047
$H_{s,t,-} = c_{s,t}(H)(H)c_{s,-} = c_{s,t}(H)(c_{s,H}),$ $H_{s,t,-} = c_{s,t}(H)c_{s,H},$ $H_{s,t,-} = c_{s,t}(H)c_{s,H},$ $H_{s,t,-} = c_{s,t}(H)(H)c_{s,-} = c_{s,H} - c_{s,H} - c_{s,H})$ $H_{s,t,-} = c_{s,t}(H)(H)c_{s,-} = c_{s,H} - c_{s,H} - c_{s,H})$ $H_{s,t,-} = c_{s,H}(H)(H)c_{s,-} = c_{s,H} - c_{s,H}(H)(H)c_{s,H}(H)(C_{s,H}(H)(H)c_{s,H}(H)(H)(C_{s,H}(H)(H)(H)(H)(H)(H)(H)(H)(H)(H)(H)(H)(H)($	ਚਦਦਦ	11.13340	*1 626 ip	c	e	29825181-	921774	0.80364	-16,183873	<i>247.0</i> 1.61.	. 127.61	52.39	58.24	26742.0	<b>9.</b> 4516#
$RC = C_{k,r}(H) - \{H\}C_{k,r} = CR$ (C - C'(s))	70	ONEC1.1.	-1.23380	¢		455.84.52H	17716.0	102/T/S	4.ECO.T1.	Ht205'91-	78.31	69'101	36.16	SHIR!	0.16123
$H_{x}^{r}(x, H)(H)(x, x, H)(H) - (x, H)$ (1.3-postiate) $-H_{x}^{r}(x, x, H)(H) = (H)(x, x, H) - (H)(H)(H)(H)(H)(H)(H)(H)(H)(H)(H)(H)(H)($	ਹ ਦ	OKEZ1'1*	N162017-	=	•	79KGZES1-	1,216.0	1950m/o	.16,899.73		64.37	£4.811	Ø.21	1.77GH	94596
$H_2C_s = C_s(H)(H)C_s = C_s(H) - C_sH_3$ (1.3-pentadiene) (C(**C,0))	3	#1626' <del>0</del> -	e	D .	•	-152.54187	12216.0	GS £27H*0	00152751-	40198'51*	72.27	£2,701	1176	1.653/48	100020
$-H_1C_4 - C_4(H) = \{H\}C_4 - C_4H_2 - \{C_3C_4\}C_4 - C_4H_2 - \{C_3C_4\}C_4 - \{C_4C_4\}C_4	ť	-0.9291R	-0,92918	e	o	-(53,4740\$	17716.0	0,81549	-16.68411	-16,49325	86.29	115.01	30,5%	1.76270	53102.0
$H_{\mu}'_{\nu} = C_{\mu}(H) - C_{\nu}H_{\mu}'_{\nu}(H) = C_{\mu}H_{\mu}'$ (1.4-prenizations) (1.7-C (e)) $-H_{\nu}'_{\nu} = C_{\nu}'(H)(H)C_{\nu} = C_{\nu}H - C_{\nu}H_{\nu}'_{\nu} = C_{\nu}'(H)(H)C_{\nu}'_{\nu} = C_{\nu}H - C_{\nu}H_{\nu}'_{\nu} = C_{\nu}'(H)(H)C_{\nu}'_{\nu} = C_{\nu}H_{\nu}'_{\nu} = C_{\nu}'(H)(H)C_{\nu}'_{\nu} = C_{\nu}'_{\nu}H_{\nu}'_{\nu} = C_$	5	-1,13340	41.920 l k	t	0	-153.674G6	1771	0,80561	-16.89873	-16. <i>507</i> 745	64.57	115,43	29.79	1,7784	96670
$H_1'' = C_k(H) - C_rH_1''(H) = C_rH_1$ $(1.4 \text{-promadiens})$ $(1.6 - C_1(e))$ $-H_2'' - H'' = C_1'(H)[H]C_r = C_rH - H_1'' - H'' - C_1'(H)[H]C_r = C_rH - H_1'' - C_1'(H)[H]C_r = C_rH - H_1'' - C_1'(H)[H]C_r = C_rH - H_1'' - C_1'(H)[H]C_r = C_rH - H_1'' - C_1'(H)[H]C_r = C_rH - H_1'' - C_1''(H)[H]C_r = C_rH - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1'' - H_1''$	ਹ ਰ	-0,929[ж	-4,929 I x	Đ	o	\$074F <b>(£</b> \$]•	17716.0	C+51H.0	. 11489'91-	-16.49325	66,53	114,01	.10.58	1.76270	033183
$-H_1C_* - H_2C_*C_*(H) = (H)C_*C_*H_2 - (\operatorname{cyclopentens})$ (C = C (e))	55.5	ятс26т	41.929.1K	a	0	\$0747631-	14416'0	0.81549	-16,6HJ1	-16 49325	36.41	8.11	26.06	1.50850	0.45116
с – н (сн.) ()	ij	-1.33%	О	a	۰	-132,74949	17716.0	0,85252	13.93955	-15.76869	77.15	10285	41.13	1882	0.1875.5
C - H (CH,)	υ	48.9 <b>2</b> 918	0	6	0 .	-152.54487	12216.0	0.80350	-15.75473	-15.56407	77.49	102.51	81'15	1,23564	0.18708
C-H (CH <sub>1</sub> ) (f)	-	A1020,0-	-41,92912	0	0	-153.47406	17716.0	OLZ [ K.O	-16.6K4F2	-16.49325	68.47	111.33	35.84	135486	0.27533
C-H (CH)	Ü	#1020:0+	-41,9291R	-0.92918	0	-154,40324	17716.0	0.77247	17,61330	-17,42244	61.10	11830	11.37	1.42088	937326

Parameters	) (a) (a) (b) (c) (b) (c) (c) (d)	(, - (, (a)	(, - (, (p)	(a)	(p)	(e) .フ~	CH, (i)	$CH_s$	CH, (ii)	H-0
	Croup	Group	Croup	Croup	Croup	Ciroup	Group	Group	Group	Croup
n,	63	-			-	1	2	3	2	1
n,	0	0	0	0	0	0	1	7	1	0
n,	0	0	0	0 .	0	0	0	0	a	0
ت	0.5	0.5	0.5	0.5	0.5	5,0	0.75	0.75	0.75	0.75
6,	0.91771	-	1		-	-	1	-	1	ı
ัง	-	_		-	_	_	-	_	I	_
· · ·	0.91771	0.91771	17719.0	17716.0	17716.0	17716.0	17716.0	17716.0	17716.0	17716.0
.5	0	0	0	0 .	-	0	1	0	1	-
3	4	2	2	2	2	2	-	-	1	1
5	0	0	0	0	٥	0	2	8	2	-
. 4	0.5	0.5	0.5	0.5	0.5	5'0	0.75	0.75	0.75	0.75
. 4	17716.0	-	-	1	-	-	-	-	_	
V, (eV)	-102.08992	-33.01226	-30, 19634	-30,19634	-30.19634	-28.79214	-72.03287	-107.32728	-70.41425	-35.12015
V (aV)	21.48386	9.83824	9.50874	9.50874	9.50874	9.33352	26.02344	38.92728	25.78002	12.87680
r (eV)	34.67062	8.63041	7,37432	7.37432	7.37432	6.77464	21.95990	32,53914	21,06675	10.48582
V_ (aV)	-17.33531	-4.31520	-3.68716	-3.68716	-3.68716	-3.38732	-10.97995	-16.26957	-10.53337	-5.24291
E(40 m) (aV)	.0	-14.63489	-14.63489	-14.63489	-14.63489	-15.56407	-14.63489	-15.56407	-15.56407	-14.63489
ΔΕ <sub>11,410</sub> (.0 m) (cV)	0	-1.85836	0	0	0	0	0	0	0	0
Er (101 10) (cV)	0	-12.77653	-14.63489	-14.63489	-14.63489	-15.56407	-14.63489	-15,56407	-15.56407	-14.63489
$\mathcal{E}_{r}[u, w] (aV)$	-63.27075	-31,63535	-31.63534	-31.63534	-31.63534	-31.63537	-49.66437	-67.69451	-49.66493	.31,63533
$E_r(u_lom - a_lom, m_sp^1, A(l))$ (eV)	-2.26759	-2.26759	-1.85836	-1.85836	-1.85836	-1.85836	0	0	0	0
E, [sn] (eV)	-65.53833	-33,90295	-33.49373	-33.49373	-33.49373	-33.49373	-49.66493	-67.69450	-49,66493	-31.63537
w (10" rad/s)	43.0680	11.0522	9.97851	23.3291	9.97851	9.43699	25.2077	24.9286	24.2751	24.1759
$E_{\kappa}$ ( $\sigma V$ )	28,34813	7,27475	6,56803	15.35563	6.56803	6.21159	16.59214	16.40846	15.97831	15.91299
ř, (εV)	-0,34517	-0.18090	-0.16982	-0.25966	-0.16982	-0.16515	-0.25493	-0.25352	-0.25017	-0.24966
Ex., (eV)	0.17897	0.14829 [48]	0.11159 [12]	0.11159	0.11159 F121	0.12312 [2]	0,35532 Eq. (13,458)	0,35532 Eq. (13,458)	0.35532 Eq. (13,458)	0.35532 Eq. (13.458
E_ (aV)	-0.25568	-0.10676	-0.11402	-0.20386	-0.11402	-0,10359	-0.07727	-0.22757	-0.14502	-0.07200
E. (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
Er kinny) (cV)	-66.04969	-34,00972	-33.60776	-33.69760	-33.60776	-33.59732	-49.81948	-67.92207	-49.80996	-31.70737
E weller in to) (cV)	-14.63489	-14.63489	-14.63489	-14.63489	-14,63489	-14.63489	-14,63489	-14.63489	-14.63489	-14.63489
Emmalle HO IN) (eV)	0	0	0	0	0	0	-13,59844	-13.59844	-13.59844	-13.59844
$E_D[imm]$ (eV)	7.51014	4.73994	4.33798	4.42782	4.18995	4.32754	7.83968	12.49186	7.83016	3,32601

Table 15.211. The total bond energies of cyclic and conjugated alkenes calculated using the functional group composition and the energies of Table 15.210 compared to the experimental values [2]. The magnetic energy E\_\_\_ that is subtracted from the

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ormula	Name	ပ "	(, = (, (a)	(e) .)−.,	(e) U-U	(p)	(e) U-U	(H, (i)	€¥2	CH, (ii)	CH	13 **	Calculated Total Bond Energy (eV)	Experimental Total Bond Energy (eV)	Relative
ž	13 Butadiene	7	-		0		0	7			2	0	42.09159	42.12705	0,00034
ž	1,3 Pentadiene	7	-	-	0	0	0	_	-	٥	0	•	54,40776	54.42484	0,00031
	1,4 Pentadiene	C)	0	0	2	0	0	<b>-</b> )	۰	_	7	٥	54.03745	54,11806	0,00149
Č.F.	1.3 Cyclopentadiene	<b>~</b> )	-	•	0	7	0	0	۰		*	۰	49.27432	49,30294	0.00058
ź	Cyclopentane	_	0	~	٥	0	7	٥	-	~	7	-	54.13565	54.86117	0.00047

						41				
Ελρ. <i>θ</i> (°)		120.9 (1,3-butadiene)	(1,3-butadiene)	(1.3-burations CCC) (1.3-burations CCC) (1.3.5-breartions CLCCc) (1.3.5-breartions CLCCc) (1.3.5-breartions CLCCc) (1.3.5-breartions CLCCc) (1.3.5-breartions CLCCc) (1.3.5-breartions CLCCc) (1.3.5-breartions CLCCc)	109.4 (1,3-cyclopentadiene)	109.3 (1,3-eyclopentadiene)	102.8 (1,3-eyclopentadiene)	110.0 (cyclopentene)	103.0 (cyclopentene)	104 0 (cyclopentene)
Cal. <i>9</i>	113.25	123,78	119.45	126.48	108.44	108.47	10241	110.14	102.85	103.61
(°)				<u> </u>						
(°)		113.23				 				ļ
(°)										
<i>Ε</i> <sub>τ</sub> (eV)	0		0	-1.85836	-1,85836	-1.85836	-1,55836	-1.85836	-1.83836	-1.85836
5p	1.17300	·	1.00000	0.83395	0.76360	0.77247_	25182.0	10.777.0	0.78620	0.79085
ر.	0.75		67.0	-		-	1	-	-	1
5			ı	-	<b>-</b> '	-	1.	<b>.</b>	1	1.
לי	-		0.75	-	-	ı	-	-	1	-
C; Alren ?	1		0.85252	0.79597	0.76360	0.77247	0.78155	0.77247	0,78155	0,79085
$\mathcal{C}_{\mathbf{i}}$	0.85252		0.85252	0,80561	0.76360	0.77247	0.78155	0.78155	0,79085	0.79085
Atom 2 Hybridization Designation (Table 15.3.A)	ж		6		34	42	38	<b>2</b> +	38	51
E metander	æ		¥.) P\$6\$6\$1-	¥).	-17.81791 C.	-17.61330 C.	-17,40869	-17.61330	-17,40869	-17,20408
Atom   Hybridization Designation (Table 15.3.A)	٥	i	٥		9	43	38	<b>8</b> 0	35	şt
Franks	-15.95955		-15.95954	-او.1888ع	-17,81791	-17.61330 (*,	-17.40869	-17,40869 C.k	-17.20409	-17.20408
2c' Terminal Abrus (u <sub>0</sub> )	3,4928		4,0000	4.6904	4,3012	43818	4,4609	4.4772	4.5166	4.5826
2¢' Ibrud 2 ( a, )	2.09132		2.09132	2.76590	2.76590	1,53321	2.86175	1,53321	2.86175	2,91548
2c' [bred ) (c, )	2,09132		2,53321	2,53321	2,53321	2,16175	2.86175	2.86175	2.91548	2 91548
المراجعة والمراجعة المراجعة والمراجعة والمراجعة والمراجعة والمراجعة والمراجع	$\angle HC_xH$ $H_1C_y=C_x$ 1,3-butadiene	$ZC_sC_sH_s$ $H_sC_s=C_s$ 1,3-butadiene	$AC_{r}C_{s}H_{s}$ $H_{s}C_{s} = C_{s}$ 1,3-butadiene	خريون ري = ديون 1,3-butadiene	کر''د'ر' ('ب = ('ر''ر' ای-cyclopentadiene	ZC,C, C,C,⇔C, L3-cyclopentadiene	$\angle C, C, C, C, \\ = C, HC, H, C, (H) = \\ 1.3-cyclopentadiene$	کل'د'ر'۔ −H <sub>3</sub> C' <sub>2</sub> H′′, هدر'بلا' <sub>3</sub> H <sub>2</sub> −− cyclopentene	$\angle C'_{1}C'_{1}C'_{2}C'_{3}C'_{4}C'_{4}C'_{5}HC'_{5}=C'_{5}H-C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{5}C'_{$	ZC,C,C, -C,H,C,H,C,H,- cyclopentene

# AROMATIC AND HETEROCYCLIC COMPOUNDS

Aromatic and heterocyclic molecules comprise at least one of an aromatic or a cyclic conjugated alkene functional group. The latter was described in the Cyclic and Conjugated Alkenes section. The aromatic bond is uniquely stable and requires the sharing of the electrons of multiple  $H_2$ -type MOs. The results of the derivation of the parameters of the benzene molecule given in the Benzene Molecule  $(C_6H_6)$  section can be generalized to any aromatic function group(s) of aromatic and heterocyclic compounds.

 $C_6H_6$  can be considered a linear combination of three ethylene molecules wherein a C-H bond of each  $CH_2$  group of  $H_2C=CH_2$  is replaced by a C=C bond to form a six-10 member ring of carbon atoms. The solution of the ethylene molecule is given in the Ethylene Molecule  $(CH_2CH_2)$  section. The radius  $r_{ethylene2sp^3}$  (0.85252 $a_0$ ) of the  $C2sp^3$  shell of ethylene calculated from the Coulombic energy is given by Eq. (14.244). The Coulombic energy  $E_{Coulomb}(C_{ethylene}, 2sp^3)$  (-15.95955 eV) of the outer electron of the  $C2sp^3$  shell is given by Eq. (14.245). The energy  $E(C_{ethylene}, 2sp^3)$  (-15.76868 eV) of the outer electron of the  $C2sp^3$  shell 15 is given by Eq. (14.246).  $E_T(C=C,2sp^3)$  (-1.13380 eV) (Eq. (14.247), the energy change of each  $C2sp^3$  shell with the formation of the C=C-bond MO is given by the difference between  $E(C_{ethviene}, 2sp^3)$  and  $E(C, 2sp^3)$ .  $C_6H_6$  can be solved using the same principles as those used to solve ethylene wherein the 2s and 2p shells of each C hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two C2sp3 hybridized orbitals 20 (HOs) to form a molecular orbital (MO) permits each participating hybridized orbital to decrease in radius and energy. Each 2sp3 HO of each carbon atom initially has four unpaired electrons. Thus, the 6H atomic orbitals (AOs) of benzene contribute six electrons and the six  $sp^3$ -hybridized carbon atoms contribute twenty-four electrons to form six C-H bonds and six C = C bonds. Each C - H bond has two paired electrons with one donated from the H AO 25 and the other from the  $C2sp^3$  HO. Each C=C bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from two sets of two  $C2sp^3$  HOs of the participating carbon atoms. Each C-H and each C=C bond comprises a linear combination

of one and two diatomic  $H_2$ -type MOs developed in the Nature of the Chemical Bond of Hydrogen-Type Molecules and Molecular Ions section, respectively.

Consider the case where three sets of C = C-bond MOs form bonds between the two carbon atoms of each molecule to form a six-member ring such that the six resulting bonds 5 comprise eighteen paired electrons. Each bond comprises a linear combination of two MOs wherein each comprises two  $C2sp^3$  HOs and 75% of a  $H_2$ -type ellipsoidal MO divided between the  $C2sp^3$  HOs:

$$\begin{pmatrix}
3(2 C2sp^3 + 0.75 H_2 MO) \rightarrow 3(C=C) - \text{ethylene-type-bond MO} \\
\rightarrow 6(C=C) - \text{bond MO of benzene}
\end{pmatrix} (15.142)$$

10 The linear combination of each H<sub>2</sub>-type ellipsoidal MO with each C2sp³ HO further comprises an excess 25% charge-density contribution per bond from each C2sp³ HO to the C = C-bond MO to achieve an energy minimum. Thus, the dimensional parameters of each bond C = C-bond are determined using Eqs. (15.42) and (15.1-15.5) in a form that are the same equations as those used to determine the same parameters of the C = C-bond MO of ethylene (Eqs. (14.242-14.268)) while matching the boundary conditions of the structure of benzene.

Hybridization with 25% electron donation to each C = C-bond gives rise to the  $C_{benzene} 2sp^3$  HO-shell Coulombic energy  $E_{(bullomb)} \left( C_{benzene}, 2sp^3 \right)$  given by Eq. (14.245). To meet the equipotential condition of the union of the six  $C2sp^3$  HOs,  $c_2$  and  $c_2$  of Eq. (15.42) for the aromatic C = C-bond MO is given by Eq. (15.62) as the ratio of 15.95955 eV, the magnitude of  $E_{Coulomb} \left( C_{benzene}, 2sp^3 \right)$  (Eq. (14.245)), and 13.605804 eV, the magnitude of the Coulombic energy between the electron and proton of  $E_{Coulomb} \left( C_{benzene}, 2sp^3 \right)$  (Eq. (14.245)).

$$C_2(benzeneC2sp^3HO) = c_2(benzeneC2sp^3HO) = \frac{13.605804 \text{ eV}}{15.95955 \text{ eV}} = 0.85252$$
 (15.143)

The energies of each C=C bond of benzene are also determined using the same equations as those of ethylene (Eqs. (14.251-14.253) and (14.319-14.333) with the parameters of benzene. Ethylene serves as a basis element for the C=C bonding of benzene wherein each of the six C=C bonds of benzene comprises (0.75)(4) = 3 electrons according to Eq. (15.142).

The total energy of the bonds of the eighteen electrons of the C=C bonds of benzene,  $E_T(C_6H_6,C=C)$ , is given by (6)(0.75) times  $E_{T+asc}(C=C)$  (Eq. (14.492)), the total energy of the C=C-bond MO of benzene including the Doppler term, minus eighteen times  $E(C,2sp^3)$  (Eq. (14.146)), the initial energy of each  $C2sp^3$  HO of each C that forms the C=C bonds of 5 bond order two. Thus, the total energy of the six C=C bonds of benzene with three electron per aromatic bond given by Eq. (14.493) is

$$E_{T}\left(C_{6}H_{6}, C=C\right) = (6)(0.75)E_{T+osc}(C=C) - (6)(3)E(C, 2sp^{3})$$

$$= (6)(0.75)(-66.05796 eV) - 18(-14.63489 eV)$$

$$= -297.26081 eV - (-263.42798 eV)$$

$$= -33.83284 eV$$
(15.144)

The results of benzene can be generalized to the class of aromatic and heterocyclic compounds.  $E_{h\nu}$  of an aromatic bond is given by  $E_r(H_2)$  (Eqs. (11.212) and (14.486)), the maximum total energy of each  $H_2$ -type MO such that

$$\bar{E}_{out} = n_1 \left( \bar{E}_D + \bar{E}_{Kvib} \right) = n_1 \left( -31.63536831 \ eV \sqrt{\frac{2\bar{E}_K}{Mc^2}} + \frac{1}{2} \hbar \sqrt{\frac{k}{\mu}} \right)$$
 (15.145)

The factor of 0.75 corresponding to the three electrons per aromatic bond of bond order two given in the Benzene Molecule ( $C_6H_6$ ) section modifies Eqs. (15.52-15.56). Multiplication of the total energy given by Eq. (15.55) by  $f_1 = 0.75$  with the substitution of Eq. (15.145) gives the total energy of the aromatic bond:

$$E_{r}(Group) = f_{1} \left( E(basis\ energies) + E_{\tau} \left( atom - atom, msp^{3}.AO \right) - 31.63536831\ eV \sqrt{\frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\epsilon_{o}R^{3}}}}{\frac{m_{e}}{m_{e}}} + n_{1}\bar{E}_{Kwib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}}} \right)$$
(15.146)

The total bond energy of the aromatic group  $E_D(Group)$  is the negative difference of the total energy of the group (Eq. (15.146)) and the total energy of the starting species given by the sum of  $c_4 E_{initial}(c_4 AO/HO)$  and  $c_5 E_{initial}(c_5 AO/HO)$ :

$$E_{D}(Group) = -\left( \int_{1}^{\infty} \left( E(basis\ energies) + E_{T}(atom - atom, msp^{3}.AO) \right) - \left( \int_{1}^{\infty} \left( \frac{E(basis\ energies) + E_{T}(atom - atom, msp^{3}.AO)}{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\epsilon_{o}R^{3}}}} \right) - \left( \frac{2\hbar\sqrt{\frac{C_{1o}C_{2o}e^{2}}{4\pi\epsilon_{o}R^{3}}}}{m_{e}} + n_{1}\bar{E}_{Kvib} + c_{3}\frac{8\pi\mu_{o}\mu_{B}^{2}}{r^{3}} \right) - \left( c_{4}E_{Initial}(AO/HO) + c_{5}E_{Initial}(c_{5}AO/HO) \right)$$
(15.147)

5 Since there are three electrons per aromatic bond,  $c_4$  is three times the number of aromatic bonds.

Benzene can also be considered as comprising chemical bonds between six CH radicals wherein each radical comprises a chemical bond between carbon and hydrogen atoms. The solution of the parameters of CH is given in the Hydrogen Carbide (CH) section. Those of the benzene are given in the Benzene Molecule  $(C_6H_6)$  section. The energy components of  $V_e$ ,  $V_p$ , T,  $V_m$ , and  $E_T$  are the same as those of the hydrogen carbide radical, except that  $E_T(C=C,2sp^3)=-1.13379~eV$  (Eq. (14.247)) is subtracted from  $E_T(CH)$  of Eq. (13.495) to match the energy of each C-H-bond MO to the decrease in the energy of the corresponding  $C2sp^3$  HO. In the corresponding generalization of the aromatic CH group, the geometrical parameters are determined using Eq. (15.42) and Eqs. (15.1-15.5) with  $E_T(atom-atom, msp^3.AO)=-1.13379~eV$ .

The total energy of the benzene C-H-bond MO,  $E_{T_{benzer}}\left(C-H\right)$ , given by Eq. (14.467) is the sum of  $0.5E_{T}\left(C=C,2sp^{3}\right)$ , the energy change of each  $C2sp^{3}$  shell per single bond due to the decrease in radius with the formation of the corresponding C=C-bond MO (Eq. (14.247)), 20 and  $E_{T_{benzer}}\left(CH\right)$ , the  $\sigma$  MO contribution given by Eq. (14.441). In the corresponding generalization of the aromatic CH group, the energy parameters are determined using Eqs. (15.146-15.147) with  $f_{1}=1$  and  $E_{T}\left(atom-atom,msp^{3}.AO\right)=\frac{-1.13379~eV}{2}$ . Thus, the energy

contribution to the single aromatic CH bond is one half that of the C=C double bond contribution. This matches the energies of the CH and C=C aromatic groups, conserves the electron number with the equivalent charge density as that of s=1 in Eqs. (15.18-15.21), and further gives a minimum energy for the molecule. Breakage of the aromatic C=C bonds to give CH groups creates unpaired electrons in these fragments that corresponds to  $c_3=1$  in Eq. (15.56) with  $E_{mos}$  given by Eq. (15.58).

Each of the C-H bonds of benzene comprises two electrons according to Eq. (14.439). From the energy of each C-H bond,  $-E_{D_{bearing}}(^{12}CH)$  (Eq. (14.477)), the total energy of the twelve electrons of the six C-H bonds of benzene,  $E_T(C_6H_6,C-H)$ , given by Eq. (14.494) 10 is

$$E_r(C_6H_6, C-H) = (6)(-E_{D_{brance}}(^{12}CH)) = 6(-3.90454 \ eV) = -23.42724 \ eV$$
 (15.148)

The total bond dissociation energy of benzene,  $E_{D}(C_{6}H_{6})$ , given by Eq. (14.495) is the negative

sum of 
$$E_T \left( C_6 H_6, C = C \right)$$
 (Eq. (14.493)) and  $E_T \left( C_6 H_6, C - H \right)$  (Eq. (14.494)):

$$E_{D}(C_{6}H_{6}) = -\left(E_{T}\left(C_{6}H_{6}, C = C\right) + E_{T}\left(C_{6}H_{6}, C - H\right)\right)$$

$$= -\left(\left(-33.83284 \ eV\right) + \left(-23.42724 \ eV\right)\right)$$

$$= 57.2601 \ eV$$
(15.149)

Using the parameters given in Tables 15.214 and 15.216 in the general equations (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)) reproduces the results for benzene given in the Benzene Molecule  $(C_k H_k)$  section as shown in Tables 15.214 and 15.216.

The symbols of the functional groups of aromatics and hertocyclics are given in Table 15.213. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and 20 energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aromatics and hertocyclics are given in Tables 15.214, 15.215, and 15.216, respectively. The total energy of benzene given in Table 15.217 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.216 corresponding to functional-group composition of the molecule. The bond angle parameters of benzene determined using Eqs. (15.79-15.108) are given in Table 15.218.

of functional groups of aromatics and hertocyclics.	Group Symbol	3, 3	() H.)
Table 15.213. The symbols of functional pr	Functional Group	CC (aromatic bond)	CH (aromatic)

rimental values [1]	· (1)			_			_
cs and hertocyclics and expe	CH Group	1.60061	1.03299	1.09327	1.101 (benzene)	1.22265	0.64517
Table 15.214. The peometrical bond parameters of aromatics and hertocyclics and experimental values [1]	U mag	1.47348	1,31468	1.39140	1.399 (benzene)	0.66540	0.89223
Table 15.214. The geometric	Parameter	0 (0,0)	c' (a,)	Bond Length 2c' (A)	Exp. Bond Length (A)	h,c (a,)	G

5 Table 15.215. The MO to HO intercept geometrical bond parameters of benzene. Ir, is E<sub>1</sub> (aran - aran, may', AO).

[Bond I: In the MO to HO intercept geometrical bond parameters of benzene. Ir, is E<sub>1</sub> (aran - aran, may', AO).

	0,21379		0.55533
	1,24678		0.75935
	38 84		8.8
	105.58	12.5	67.79
	74.42	21.71	***
	-16.90248	\$7000 91*	
	-17.09334	-17 09334	
	0.79597	0.79597	
Ļ	4	0.91771	
trees to		-153.88327	
٠			
0.36690		0.56690	
-0 85035		-0.85005	
-0.85035		-0.83033	
÷	;	۲	
( - H (CH)	2 34 7	. −m., =t	
	-0 85035 -0.56690 0 153 EPUS - TERRITOR -	-0 85035 -0 56690 0 -153,00277 0,91771 -0,795934 -16,90248 74,42 105,58 38 84 1,2467B	-0.85035 -0.56590 0 -1.53.55027 0.91771 0.79597 -1.709334 1.6.90248 74,42 105.58 38.84 1.24678 -0.85035 0.56659 0 -1.53.8327 0.95957 1.709334 1.80.928 13.84

Table 15.216. The energy parameters (eV) of functional groups of aromatics and hertocyclics.

Table 15.210. The energy parameters (c	C=C	СН
Parameters	Group	Group
$f_1$	0.75	1
$n_{i}$	2	· 1
$n_2$	0	0
$n_3$	0	0
$C_1$	0.5	0.75
$C_2$	0.85252	1
c <sub>1</sub>	1	1
<i>c</i> <sub>2</sub> .	0.85252	0.91771
$c_3$	0	1
<i>c</i> <sub>4</sub>	3	1
<i>c</i> <sub>s</sub> .	. 0	1
$C_{_{1o}}$	0.5	0.75
C <sub>20</sub>	0.85252	1
$V_{c}(eV)$	-101.12679	-37.10024
$V_{p}(eV)$	20.69825	13.17125
T (eV)	34.31559	11.58941
$V_{m}$ (eV)	-17.15779	-5.79470
E(AOIHO) (eV)	0	-14.63489
$\Delta E_{H_1MO}(AOIHO)$ (eV)	0	-1.13379
$E_r$ (ADIHO) (eV)	0	-13.50110
$E_T(H_1MO)$ (eV)	-63.27075	-31.63539
$E_r(atom-atom, msp^3.AO)$ (eV)	-2.26759	-0.56690
$E_{T}(MO)$ (eV)	-65.53833	-32.20226
$\omega \left(10^{15} \ rad \ / \ s\right)$	49.7272	26.4826
$E_{\kappa}$ $(eV)$	32.73133	17.43132
$\overline{E}_{D}$ (eV)	-0.35806	-0.26130
$\overline{E}_{\kappa_{vib}}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)
$\overline{E}_{oc}$ (eV)	-0.25982	-0.08364
$E_{mag}$ (eV)	0.14803	0.14803
$E_r(Group)$ $(eV)$	-49.54347	-32.28590
$E_{lninal}(c_{i}$ AOIHO) (eV)	-14.63489	-14.63489
$E_{lnitial}(c_s AOIHO) (eV)$	0	-13.59844
$E_{D}(Group)$ $(eV)$	5.63881	3.90454

Table 15.217. The total bond energies of benzene calculated using the functional group composition and the energies of Table 15.216 compared to the experimental values [2].

				Cal. 6	>		120,19	
				6 3	2			
				6.0	2			
				<i>e</i> , @	=			
				ey E			-1.63536	
			-	∿-		- FEEDE 0	0.79634	
·[7]				ت		-	-	
micing val				ບ"		-		
				<u>ت</u>		-		
				Ates 5.		0.79232		
			Į,	, way		0.79232	-	
Relative  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error  Error	0 00000	om, mxp³.40}.	Atom 2	Hybri dizznioa Designation	(Table (5.3.A)	34		
Experimental Total Bond Energy	57,26340	E, (atom – a		Aires 2		-17 L721R		
Calculated Total Bond Tot	57.26008	Table 15.218. The bond angle parameters of benzene and experimental values [1]. $E_{r}$ is $E_{r}$ (anm – anm, msp.'.AO).	Atom I	Hybridization Designation	(Table 15.3.A)	7		
<b>*</b>		xperimental	E	Alma I		-17.17218		
ť		ene and e	. JC	Teminal Aisen	2	4.55%5		
Cac	,	's of benz	2c'	(a)		2.62936		
		c paranete	,2C.	(°		2.62936 2.62936 4,55%5		_
Name	뫄	The bond angl	Angle			tic)	#	Tic)
Formula	C.H. Bonzeno	Table 15.218.	Atoms of Angio		1.37	(aromatic)	H:3.)7	(arom.

#### NAPHTHALENE

Naphthalene has the formula  $C_{10}H_8$  and comprises a planar molecule with two aromatic rings that share a common C-C group. In order to be aromatic, the total number of bonding electrons must be a multiple of 3 since the number of electrons of the aromatic bond is (0.75)(4)=3 as shown in the Benzene section. In the case of naphthalene, the peripheral 10 carbons form the aromatic MO with the center bridged by a C-C single bond. Then, 30 electrons of the 48 available form aromatic bonds, two electrons form the bridging C-C single bond, and 16 electrons form the eight C-H single bonds. The energies of the aromatic carbons are given by the same equations as those of benzene (Eqs. (15.42), (15.1-15.5), and (15.146-15.147)), except that there are 10 in naphthalene versus six in benzene. Since there are three electrons per aromatic bond,  $c_4$  is three times ten, the number of aromatic bonds. Similarly, the aromatic C-H group of naphthalene is equivalent to that of benzene.

To meet the equipotential condition of the union of the ten  $C2sp^3$  HOs bridged by the C-C single bond, the parameters  $c_1$ ,  $c_2$ , and  $c_3$  of Eq. (15.42) are one for the C-C group, 15  $C_{10}$  and  $C_{11}$  are 0.5, and  $c_{12}$  given by Eq. (15.142) is  $c_{12}(C2sp^3HO) = 0.85252$ . Otherwise, the solutions of the C-C bond parameters are equivalent to those of the replaced C-H groups with  $E(AO/HO) = -14.63489 \, eV$  and  $\Delta E_{H_1MO}(AO/HO) = -1.13379 \, eV$  in Eq. (15.41). Similarly, the energy parameters are determined using Eqs. (15.52-15.56) with  $E_T(atom-atom, msp^3AO) = \frac{-1.13379 \, eV}{2}$ .

The symbols of the functional groups of naphthalene are given in Table 15.219. The corresponding designation of the structure is shown in Figure 62. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of naphthalene are given in Tables 15.220, 15.221, and 15.222, respectively. The total energy of naphthalene given in Table 15.223 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.222 corresponding to functional-group composition of the molecule. The bond angle parameters of naphthalene determined using Eqs. (15.79-15.108) are given in Table 15.224.

ı								,			
Group Symbol	) # C		8	Toble 15, 220. The neometrical bond parameters of naphthalene and experimental values [1].	C-C Group	1.75607	1,32517	1,40250	1,42 (naphthatene)	1.15226	0.75462
Table 15.219. The symbols of functional process of machine Group  Functional Oroup				rameters of naphth	Crowp	1,60061	1,03299	1,09327	1,101 (benzene)	1.22265	0.64537
Functional Group	ভ	(puo	,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	geometrical bond pa	O all o	1.47348	1,31468	139140	1.40 (avg.) (naphthalene)	0.66540	0.89223
Functio	C.C. (aromaño bond)	CH (groundie)	ביי ומוחפייים	rotte 15 220. The	Parainder	0 (0,)	c. (a)	Bond Length	Exp. Bond Length	6.5 (0.)	(6)

		9	onehthalens F	LIA. TIM, HIGH - HOLD - HOLD AND THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE OF THE STATE O	OBLUST AND				1	-	į	4	•	9	5
Table 15.221. The MO to HO intercept geometrical bond parameters of the	etrical bon	parameters of	tapillitature, or		,	Finel Total			£ (014)	E(C240)	<b>D</b>	5	5 3	- (	( )
Bond	Atom	Er (eV)	(e.V.)	(e, t,	. (§ 't	Energy	ો જે	· (°	(eV)	(eV) Final	 ©	 ©	 E	<u>,</u>	3)
	_	Bond	Bond 2	Bond 3	+ puch										0.576.0
						(ev)			12 00114	-16.90248	74.17	105.58	33.84	1,24676	0.613.0
	I			00000	_	-153,88327	0.91776	0.79397	- C.C						455533
(8.7) 17 . 3	·	-0.85035	-0.85035	0.300.0	,				7.500.5.	TACOD AL	134.24	45.76	58.98	0.75935	20000
1000				000000	e	-153.ER327	177.16,0	0.79597	*CC60'/1-			1			
2.	υ U	-0.85035	-0.85035	04806'0-						100000	12021	45.19	\$9.66	0.74430	0.57038
C=HC =C				***************************************	•	.153.59983	122160	0.80939	-16.80919	DE 10.01-					
* *	۔ ن	4.8.035	20,85035	0,28343	•					0017	9 80	30.50	47.66	1.18169	1474
)=('U')=U					•	141 59983	122160	0.80739	-16.80939	-16.01901	200				
		-0.85035	26052.0-	-0,28345			7								
(:)															

Table 15.222. The energy parameters (eV) of functional groups of naphthalene.

Parameters	C = C	СН	C-C
•	Group	Group	Group
$f_1$	0.75	1	1
$n_{\rm l}$	2	1	1
<i>n</i> <sub>2</sub>	0	0	0
<i>n</i> <sub>3</sub>	0	0 -	0
$C_1$	0.5	0.75	0.5
<i>C</i> <sub>2</sub>	0.85252	1	1
<i>c</i> <sub>1</sub>	1	1	1
$c_{2}$	0.85252	0.91771	0.85252
<i>c</i> <sub>3</sub>	0	1	0
<i>c</i> <sub>4</sub>	3	1	2
<i>c</i> <sub>5</sub>	0	1	0
$C_{\mathbf{l}_{\boldsymbol{v}}}$	0.5	0.75	0.5
$C_{2o}$	0.85252	1	1
$V_a$ (eV)	-101.12679	-37.10024	-34.43791
$V_{p}(eV)$	20.69825	13.17125	10.26723
T (eV)	34.31559	11.58941	9.80539
$V_{\rm m}$ (eV)	-17.15779	-5.79470	-4.90270
$E($ логн $\omega)$ (e $V$ )	0	-14.63489	-14.63489
$\Delta E_{H_2MO}$ (AOI HO) (eV)	0	-1.13379	-1.13379
$E_{T}(AOIHO)$ (eV)	0	-13.50110	-13.50110
$E_T(H_1MO)$ (eV)	-63.27075	-31.63539	-31.63529
$E_r(atom-atom, msp^3.AO)$ (eV)	-2.26759	-0.56690	-0.56690
$E_{T}(MO)$ (eV)	-65.53833	-32.20226	-32,20226
$\omega \left(10^{15}  rad  l  s\right)$	49.7272	26.4826	23.6343
$E_{\kappa}$ (eV)	32.73133	17.43132	15.55648
$\overline{E}_{D}$ $(eV)$	-0.35806	-0.26130	-0.25127
$\widetilde{E}_{Kvib}$ $(eV)$	0.19649 [49]	0.35532 Eq. (13.458)	0.12312
$\bar{E}_{asc}$ (eV)	-0.25982	-0.08364	-0.18971
$E_{\text{mag}}$ (eV)	0.14803	0.14803	0.14803
$E_r(Graup)$ (eV)	-49.54347	-32.28590	-32.39198
$E_{initial}(c, AOIHO) (eV)$	-14.63489	-14.63489	-14.63489
Emilial (c, AUIRO) (eV)	0	-13.59844	0
$E_{D}^{(Group)}$ (eV)	5.63881	3.90454	3.12220

Table (5.223. The total bond energies of raphthalene calculated using the functional group composition and the energies of Table 15.222 compared to the experimental values [2].

Checken's Experiment Relations

0.00049	C, C, C, C, O, O, O, O, O, O, O, O, O, O, O, O, O,	6, C, C, C, C, C, C, C, C, C, C, C, C, C,	6, 6, 6, 6, 6, 6, 6, 6, 6, 6, 6, 6, 6, 6
I experimental values [1]. E, is $E_r$ (atom – atom, nxp'. AO).	0.79232	0.79232	0.79232
5.	0.79232	0.79232	0.79232
C <sub>1</sub> C <sub>1</sub>	0.79232	0.79232	0.79232
G <sub>1</sub> G <sub>2</sub>			

# **TOLUENE**

Toluene has the formula  $C_7H_8$  and comprises the benzene molecule with one hydrogen atom replaced by a methyl group corresponding to a  $CH_3$  functional group and a C-C functional group. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The  $CH_3$  functional group is the same as that of continuous and branched-chain alkanes given in the corresponding sections.

The bond between the methyl and aromatic ring comprises a C-C functional group that is are solved using the same principles as those used to solve the alkane functional groups wherein the 2s and 2p AOs of each C hybridize to form a single  $2sp^3$  shell as an energy 10 minimum, and the sharing of electrons between two  $C2sp^3$  HOs to form a MO permits each participating hybridized orbital to decrease in radius and energy. To match energies within the MO that bridges methyl and aromatic carbons, E(AO/HO) and  $\Delta E_{H_1MO}(AO/HO)$  in Eq. (15.41) are -15.35946 eV (Eq. (14.155)) and  $\frac{-1.13379 \text{ eV}}{2}$ , respectively.

To meet the equipotential condition of the union of the aromatic and methyl  $C2sp^3$  HOs of the C-C single bond, the parameters  $c_1$ ,  $c_2$ , and  $c_3$  of Eq. (15.42) are one for the C-C group,  $c_{10}$  and  $c_{11}$  are 0.5, and  $c_{12}$  given by Eq. (13.430) is  $c_{12}(C2sp^3HO) = 0.91771$ . To match the energies of the functional groups,  $c_{12}(C2sp^3HO) = 0.91771$ . To match (15.52) due to the charge donation from the  $c_{12}(C2sp^3HO) = 0.91771$ . Which is the same energy per  $c_{12}(C2sp^3HO) = 0.91771$ .

The symbols of the functional groups of toluene are given in Table 15.225. The corresponding designation of the structure is shown in Figure 63. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of toluene are given in Tables 15.226, 15.227, and 15.228, respectively. The total energy of toluene given in Table 15.229 was calculated as the sum over the integer multiple of each  $E_D(G^{roup})$  of Table 15.228 corresponding to functional-group composition of the molecule. The bond angle parameters of toluene determined using Eqs. (15.79-15.108) are given in Table 15.230.

Table 15.226. The peronetrical bond parameters of folluene and experimental values [1].

Perameter C=C CH (i) (:-C C-H (i:H<sub>1</sub>))

Group Group Group Group Group

a (a<sub>1</sub>) 1.41348 1.50061 2.06004 1.64920

c' (a<sub>1</sub>) 1.31468 1.03299 (.43528 1.04856

Table 15.225. The symbols of functional groups of Toluene.

Group Symbol.

C. C. C. (aromatic bond)

C. C. (C. (r.), (c. 4.6)

C. C. (c. 4.6)

C. C. (c. 4.6)

CH, group

C=C CH (6) C-C C-H (CH,)

1,10974

1,51904

1.09327

1,39140

c (a<sub>4</sub>)
Bond Length
Length
Length
(A)

1.524 (toluene)

1,11 (avg.) (toluene) 1,22265 0,15511

(a, t, d,

0.55533

0,37901

**6/1252.0** 

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$
First Total
Final Total (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0) (2,0)
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Final Total   F.   F.   F.   F.   F.   F.   F.   F
Final Total Energy (C2) (eV) (eV) (151.8327 (151.8327 (151.8327 (151.8327)
Final Total Energy C2xy (C2xy (Ex) 1.13.18327 1.153.8827 1.151.8827 1.151.8827
of toluene. E <sub>t</sub> is E <sub>t</sub> (atom - atom, map <sup>3</sup> AO).  of toluene. E <sub>t</sub> is E <sub>t</sub> (atom - atom, map <sup>3</sup> AO).  (eV) (eV) (eV) (eV)  Bond 2 (eV) (eV)  0 0 0 0  0 0 0  0 0 0  0 0 0  0 0 0  0 0 0  0 0 0  0 0 0  0 0 0  0 0 0  0 0 0  0 0 0  0 0 0  0 0 0  0 0 0  0 0 0  0 0 0  0 0 0  0 0 0  0 0 0  0 0 0  0 0 0
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1,27295 0,63380 of toluene. £, is £, \$\frac{F_T}{V}\$ (eV) Bond 2 0 0.035033
1,41774 0,69673 d parameters (eV) Bond 1 0,3669 0,38699 0,36690
33 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
1.22265 0.64533
11 The MO to HC (", H,
$\begin{array}{c c} (A) & \\ h, c (a_a) & \\ \hline & & \\ & c \\ \hline & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\$

Table 15.228. The energy parameters (eV) of functional groups of toluene.

Parameters	C=C	CH (i)	C-C	CH <sub>3</sub>
Tarameters	Group	Group	Group	Group
<i>f</i> <sub>1</sub>	0.75	1		
<i>n</i> <sub>1</sub>	2	1	1	3
n <sub>2</sub>	0	0	0	2
n <sub>3</sub>	0	0	0	0
$C_{_{1}}$	0.5	0.75	0.5	0.75
$C_2$	0.85252	1	1	1
$c_{i}$	1	1	ı	1
<i>c</i> <sub>2</sub>	0.85252	0.91771	0.91771	0.91771
<i>c</i> <sub>3</sub>	0	1	0	0
C <sub>4</sub>	3	1	2	1
<i>c</i> <sub>s</sub>	0 .	1	0	3
$C_{io}$ .	0.5	0.75	0.5	0.75
C <sub>20</sub>	0.85252	1	1	1
V <sub>*</sub> (eV)	-101.12679	-37.10024	-29.95792	-107.32728
$V_{p}(eV)$	20.69825	13.17125	9.47952	38.92728
T(eV)	34.31559	11.58941	7.27120	32.53914
$V_{m}(eV)$	-17.15779	-5.79470	-3.63560	-16.26957
E(AOLHO) (eV)	0 .	-14.63489	-15.35946	-15.56407
$\Delta E_{H_1MO}(AOIHO) (eV)$	0	-1.13379	-0.56690	0
$E_r(AOIHO) \cdot (eV)$	0	-13.50110	-14:79257	-15.56407
$E_{T}(H_{i}MO)$ (eV)	-63.27075	-31.63539	-31.63537	-67.69451
$E_r(atom-atom, msp^3.AO)$ (eV)	-2.26759	-0.56690	-1.13379	0
$E_{r}(MO)$ $(eV)$	-65.53833	-32.20226	-32.76916	-67.69450
$\omega \left(10^{15} \ rad \ / \ s\right)$	49.7272	26.4826	16.2731	24.9286
$E_{\kappa}$ (eV)	32.73133	17.43132	10.71127	16.40846
$\overline{E}_{_{D}}$ (eV)	-0.35806	-0.26130	-0.21217	-0.25352
$\overline{E}_{Kvib}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.14940 [53]	0.35532 (Eq. (13.458))
$\vec{E}_{osc}$ (eV)	-0.25982	-0.08364	-0.13747	-0.22757
$E_{mag}$ (eV)	0.14803	0.14803	0.14803	0.14803
$E_{r}(Group)$ (eV)	-49.54347	-32.28590	-32.90663	-67.92207
$E_{initial}(\epsilon, AOIHO) (eV)$	-14.63489	-14.63489	-14.63489	-14.63489
E <sub>initial</sub> (c <sub>s</sub> AOI HO) (eV)	0	-13.59844	0	-13.59844
$E_D(Grap)$ (eV)	5.63881	3.90454	3.63685	12.49186

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Formula Name C=C (:H (i) C-(') Total Experimental values [2].  C-H Total Experimental values [2].  Table 15.230. The bond angle parameters of foliuene and experimental values [1]. E <sub>7</sub> is E <sub>7</sub> (ann - ann, mxp².AC).  Annual Annual (a) (a) (a) (a) (a) (a) (b) (b) (c) (c) (c) (c) (c) (c) (c) (c) (c) (c							T.	<u> </u>	
Formula Name C=C CH (i) C-('H') Total group composition and the energies of Table 15.228 compared to the experimental values [2].  CH. Total and the energies of Table 15.228 compared to the experimental values [2].  Table 15.230. The bond angle parameters of folluene and experimental values [1]. E, is E, (atom - atom, may) AO).  Atom 1							.3	•	_
Formula Name C=C (H (i) C-(') Total group composition and file energies of Table 15.228 compared to the experimental value C=C (H (i) C-(') Total Boad Boad Total Boad Total Boad Boad Boad Beginson Energy left)  Table 15.230. The bond angle parameters of foliuene and experimental values [1]. E, is E <sub>T</sub> (ann - ann, mxp².AC).  Along Anna (a) (a) (a) Anna Anna (b) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c) Anna (c)	E	[2] 88					ű		
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Formula Name C"C"  CH. Tolone 6  Table 15.230. The bond angle parameters of toluene and expression for the bond (a) 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	using the f	€			erimental	L	Alver		ĺ
Formula Name C=C C C C FH. Toluene 6  Table 15.230. The bond angle parameters of tolue (a) [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5] [1.5]	calculated	Ð			ene and ex	,,,,	Toronto.	(0)	
Formula Name  Cyl. Tolone  Table 15.230. The bond angle paranet  Ammericance Co.	of toluene	ں ۳ باہد	9		ers of tolu	3,0	, .	60	
Formula Name CyH, Tolume Table 15,230, The bond ang	d chergies				le paramet	20.	The state of	9	
Formula Cyff. Tolone Table 15230. Th	e total bon	Nante			e bond ang				
Formult C,H,	7.777		Toluene		5.230. Th	Cleans of Ang			
	200	Formul	3		Table				

# **CHLOROBENZENES**

Chlorobenzenes have the formula  $C_6H_{6-m}Cl_m$  and comprise the benzene molecule with at least one hydrogen atom replaced by a chlorine atom corresponding to a C-Cl functional group. The aromatic C=C and C-H functional groups are equivalent to those 5 of benzene given in Aromatic and Heterocyclic Compounds section.

The small differences between energies of ortho, meta, and para-dichlorobenzene is due to differences in the energies of vibration in the transition state that contribute to  $E_{asc}$ . Two types of C-Cl functional groups can be identified based on symmetry that determine the parameter R in Eq. (15.48). One corresponds to the special case of 1,3,5 substitution and the other corresponds to other cases of single or multiple substitutions of Cl for H. P-dichlorobenzene is representative of the bonding with R=a. 1,2,3-trichlorbenzene is the particular case wherein is R=b. Also, beyond the binding of three chlorides  $E_{mag}$  is subtracted for each additional Cl due to the formation of an unpaired electrons on each C-Cl bond.

15 The bond between the chlorine and aromatic ring comprises two C-Cl functional groups that are solved using the same principles as those used to solve the alkyl chloride functional groups as given in the corresponding section wherein the 2s and 2p AOs of each C hybridize to form a single 2sp3 shell as an energy minimum, and the sharing of electrons between the C2sp3 HO and Cl AO to form a MO permits each participating hybridized 20 orbital to decrease in radius and energy. As in the case of alkyl chlorides,  $c_2$  of Eq. (15.52) for each C-Cl-bond MO is one, and the energy matching condition is determined by the  $C_2$ parameter given by Eq. (15.111) which is  $C_2(C2sp^3HO\ to\ Cl) = 0.81317$ . To match energies within the MO that bridges the chlorine AO and aromatic carbon C2sp3 HO, E(AO/HO) and  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) are -14.63489 eV and -2.99216 eV, 25 respectively. The latter matches twice that of the replaced C-H-bond MO plus  $E_r(atom-atom, msp^3.AO)$ . To match the energies of the functional groups,  $E_T(atom-atom, msp^3.AO)$  of the C-Cl-bond MO in Eq. (15.53) due to the charge donation from the C and Cl atoms to the MO is  $-0.72457 \, eV$  (Eq. (14.151)).

The symbols of the functional groups of chlorobenzenes are given in Table 15.231. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of chlorobenzenes are given in Tables 15.232, 15.233, and 15.234, respectively. The total energy of each chlorobenzene given in Table 15.235 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.234 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(Group)$  (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of chlorobenzenes determined using Eqs. (15.79-15.108) are given in Table 15.236.

Table 15.231. The symbols of functional groups of chlorobenzenes.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH (i)
Cl-C (Cl to aromatic bond)	C-Cl (a)
Cl - C (Cl to aromatic bond of 1,3,5-trichlorbenzene)	C – CI (b)

Bond Provided the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Con				Try to try will	" deminion	, .									
· gu	Atom	(eV) Bond (	(eV) Bond 2	(eV) Bond 3	<i>Ε<sub>τ</sub></i> (eV) Bond 4	Final Total Energy C'249	ê{	(a) 1°	(c2p) (eV) Final	E(C24p²)	(a)	هـ ۍ	هر ٦	(a, a,	(o°)
C-H(C,H).	?	-0.85015	7 26034 C	24600	,	16.47								_	
y K		0.0000		0.0000		-153,88327	17716'0	0.79597	-17.09334	-16.90248	74,42	105.58	38.84	1.24678	0.21379
('=HC'=C	,,	0.8503.5	-0.85035	-0.56690 .		-153.88327	0.91771	0.79597	-17.09334	-16.90248	134.24	43.76	89,88	0.75935	cress o
(c=)(r,-a		-0.36229	-0.85015		0 .	153.67867	0.91771	0.80561	-16.88873	-16 69786	מנמי	106.68	31.67	1.8791	0.731.70
( ) /: /::															į
C= C - C7	C	-0.36229	. 0	0	0		1.05158	0.19582	15.18804		82.92	97.08	37.22	1.75824	0.11042
$C_{\lambda} = (C_{\lambda})C_{\lambda} = C_{\lambda}$ $(C_{\lambda} \text{ bound to } H \text{ or } C_{\lambda})$	٠ ,٥	-0.36229	-0.85035	\$1058.0-	0	-153.67867	0.91771	0.80561	-16.88873	-16.69716	134.65	\$ SUS	59.47	0.74854	0.36614

		E + 4 ! 1	
 A THO CHICKET DE	11 MILLOUGE S & C A	TO HUNCHODAL	groups of chlorobenzenes.

Parameters	C=C	CH (i)	C-Cl (a)	C-Cl (b)
	Group	Group	Group	Group
$f_1$	0.75	1		
n,	2	1	1	1
η <u>.</u>	0 .	0	0	0
<i>n</i> <sub>3</sub>	0	0	0	0
$C_{\mathbf{i}}$	0.5	0.75	0.5	0.5
C <sub>2</sub>	0.85252	1	0.81317	0.81317
<i>c</i> <sub>1</sub>	1	]	1	1
<i>c</i> <sub>2</sub>	0.85252	0.91771	1	1
<i>c</i> <sub>2</sub> .	0	1	. 0	0
<i>c</i> <sub>4</sub>	3	J	2	2
<i>c</i> <sub>3</sub>	0	1	0	0
C <sub>10</sub>	0.5	0.75	0,5	0.5
C <sub>20</sub>	0.85252	1	0.81317	0.81317
V (eV)	-101.12679	-37.10024	-31.85648	-31.85648
V, (eV)	20.69825	13,17125	8.25686	8.25686
T (eV)	34.31559	11.58941	7.21391	7.21391
$V_m$ (eV)	-17.15779	-5.79470	-3.60695	-3.60695
E(лоіно) (el')	0	-14.63489	-14.63489	-14:63489
$\Delta E_{H_2MO}(MOINO)$ (eV)	0	-1.13379	-2.99216	-2.99216
$E_{\gamma}(AOIHO)$ (eV)	0	-13.50110	-11.64273	-11.64273
$E_{T}(H_{2}MO)$ (eV)	-63.27075	-31.63539	-31.63539	-31.63539
$E_{\tau}(atom-atom, msp^3.AO)$ (eV)	-2.26759	-0.56690	-0.72457	-0.72457
$E_{r}(MO)$ (eV)	-65.53833	-32.20226	-32.35994	-32.35994
$\omega \left(10^{15} \ rad \ / \ s\right)$	49.7272	26.4826	8.03459	14.7956
$E_{K}$ (eV)	32.73133	17.43132	5.28851	9.73870
$\bar{E}_n$ (eV)	-0.35806	-0.26130	-0.14722	-0.19978
$\overline{E}_{K_{PP}}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.08059 [12]	0.08059
$\tilde{E}_{osc}$ (eV)	-0.25982	-0.08364	-0.10693	[12] -0.15949
$E_{meg}$ (eV)	0.14803	0.14803	0.14803	0.14803
$E_r(Group)$ (eV)	-49.54347	-32.28590	-32.46687	-32.51943
E <sub>inited</sub> (c. AOIHO) (eV)	-14.63489	-14.63489	-14.63489	-14.63489
E <sub>mileol</sub> (c, 1011HO) (eV)	0	-13.59844	0	0
$E_D(Grap)$ (eV)	5.63881	3.90454	3.19709	3.24965

Communic)	∠('C(' (aromatic)	Verme of Angly
	2.62936	2c'  lend    (a <sub>n</sub> )
	2.62936	2c' Hend 1 (o,)
	4.5585	2c Ternial Atons (a <sub>a</sub> )
	4.585 -17.17218	Erronbanke: Alem I
	¥	Atom 1 Hybridization Designation (Trible 153.A)
	-17.17218	E Castombe Ason 2
	3,	. Atom 2 Hybridization Designation Table 15.3.A)
	0.79232	C <sub>3</sub>
	0.79232	C <sub>3</sub>
	-	C,
	-	. c,
	_	
	0.79232	ć.
	-1.85836	Ε <sub>τ</sub> (eV)
		(), e
120,19		() ,0
		. O.
16'61	120.19	Cal. θ (*)
120 [50-52] (benzene)	120 (∠CC(H)C chlorobenzene) 121.7 (∠CC(C)C chlorobenzene) 120 (\$0-32) (benzene)	Exp. θ (°)

of the  $E_{D}$  (www) (vV) values based on composition is given by (15.58). Table 15.233. The total bond energies of chlorobenzenes calculated using the functional group composition and the energies of Table 15.234 compared to the experimental values (2). The magnetic energy  $E_{neg}$  that is subtracted from the weighted sum

C=C

CH (i)

Croup (2)

C'~(1) (b) Group

# PHENOL

Phenol has the formula  $C_6H_6O$  and comprises the benzene molecule with one hydrogen atom replaced by a hydroxyl corresponding to an OH functional group and a C-O functional group. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The OH functional group is the same as that of alcohols given in the corresponding section.

The bond between the hydroxyl and aromatic ring comprises a C-O functional group that is are solved using the same principles as those used to solve the alcohol functional groups wherein the 2s and 2p AOs of each C hybridize to form a single  $2sp^3$  10 shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and O AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. In aryl alcohols, the aromatic  $C2sp^3$  HO has a hybridization factor of 0.85252 (Eq. (15.143)) with an initial energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)) and the O AO has an energy of  $E(O) = -13.61806 \, eV$ . To meet the equipotential condition of the union of the C-O  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.52) for the C-O-bond MO given by Eqs. (15.68) and (15.70) is

$$c_{2}(arylC2sp^{3}HO \ to \ O) = \frac{E(O)}{E(C,2sp^{3})}c_{2}(arylC2sp^{3}HO)$$

$$= \frac{-13.61806 \ eV}{-14.63489 \ eV}(0.85252)$$

$$= 0.79329$$
(15.150)

 $E_T(atom-atom, msp^3.AO)$  of the C-O-bond MO in Eq. (15.52) due to the charge donation from the C and O atoms to the MO is  $-1.49608 \, eV$ . It is based on the energy match between the OH group and the  $C2sp^3$  HO of an aryl group and is given by the linear combination of  $-0.92918 \, eV$  (Eq. (14.513)) and  $-1.13379 \, eV$  (Eq. (14.247)), respectively.

The symbols of the functional groups of phenol are given in Table 15.237. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of phenol are given in Tables 15.238, 15.239, and 15.240, respectively. The total energy of phenol given in Table 15.241 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.240

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corresponding to functional-group composition of the molecule. The bond angle parameters of phenol determined using Eqs. (15.79-15.108) are given in Table 15.242.

Table 15.237. The symbols of functional groups of phenol.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH (i)
Aryl C-O	C-O (a)
OH group	• ОН

Table 15.238. The geometrical bond parameters of phenol and experimental values [1].

14010 13.230.	ne geometrear oc	na parameters or i		
Parameter	C = C Group	CH (i) Group	C – O (a) Group	<i>OH</i> Group
$a(a_0)$	1.47348	1.60061	1.68220	1.26430
$c'(a_0)$	1.31468	1.03299	1.29700	0.91808
Bond Length $2c'(A)$	1.39140	1.09327	1.37268	0.971651
Exp. Bond Length (Å)	1.397 avg. (phenol)	1.084 (phenol)	1.364 (phenol)	0.956 (phenol)
$b,c(a_0)$	0.66540	1.22265	1.07126	0.86925
е	0.89223	0.64537	0.77101	0.72615

Table 15.239. The MO to HO intercept geometrical bond parameters of phenol. $E_t$ is $E_t$ (atom - atom, axp. AO)	geometrical boo	d parameters of	phenol. E, is a	i, (atom – atom,	mip AO)										
Bond	Atom	4,	£3	$\mathcal{L}_{r}$	E,	Final Total	, mend	r famel	E (C2p")	E(C28p)	6,	θ	е,	'h	4,
		· (eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	t:nengy ('2 <i>sp</i> ' (eV)	(a.)	$(a_{\nu})$	(eV) Final	(eV) Final	3	3	3	(a,)	(a <sub>a</sub> )
C-H(C'H)	, c.	-D.X5033	-0.85035	0.36690	0	-153.88327	11,168	0.79597	-17.09334	-16,90248	74,42	105.58	71.15	1.24578	0.21379
$\left(C_{s}^{+}\right)_{c}C_{s}\mathcal{O}-H$	0	-0,74804	0	0	o		1.00000	0,87363	-15.57379		115.79	1519	64.82	CVTELO	0.38009
$\left(C^* = \int_{\mathcal{X}} C^* - OH\right)$	.,	-0.7480-4	-0.83033	-0.N.JOJS	0	-134,06442	0.91771	0.72762	-17.27448 .	-17,08362	100.00	80,00	46.39	1.16026	0.13674
$HO^{-n}(\mathbb{R}^n)$	. 0	-0,74804	u	Q.	0		1 09000	0.87363	15.57379		106.51	73,49	\$1.43	1.04871	0.24829
$\left(C_{x}^{+}\right)^{2}$	ر:	-0.74804	-0.85035	-0.H503\$	0	-154.06442	0.91771	0.71762	-17.27adX	-17.08362	133.11	46,12	38.33	0.76870	0.54598
$HO^{*}_{\infty}(H)C^{*}_{\infty})$	Ç	\$105%11-	\$105%.	-0.56690	9	-153,88327	0.91771	0.79597	-[7.09334	-16.90248	134,24	45.76	86.85	0.75935	0.55533

Table 15.240. The energy parameters (eV) of functional groups of phenol.

Table 15.240. The energy parameter	ers (e v ) or runci	1		077
Parameters	C=C Group	CH (i) Group	<i>C − O</i> (a) Group	<i>OH</i> Group
$f_1$	0.75	1		
n	2	1	1	1
$n_2$	0	0	0	0
$n_3$	0	0	0	0
<i>C</i> ,	0.5	0.75	0.5	0.75
$C_1$	0.85252	1	1	1
<i>c</i> ,	1	1	1	0.75
<i>c</i> ,	0.85252	0.91771	0.79329	1
<i>c</i> ,	0	1	0	1
C,	3	1	2	]
c,	0	1	0	1
C <sub>10</sub>	0.5	0.75	0.5	0.75
C <sub>20</sub> ····	0.85252	. 1	1 .	1
V (eV)	-101.12679	-37.10024	-34.04658	-40.92709
$V_{p}(eV)$	20.69825	13.17125	10.49024	14.81988
T (eV)	34.31559	11.58941	10.11966	16.18567
V <sub>n</sub> (eV)	-17.15779	-5.79470	-5.05983	-8.09284
E(логно) (eV)	0	-14.63489	-14.63489	-13.6181
$\Delta E_{H_2MO}(AO(HO))$ (eV)	0	-1.13379	-1.49608	0
$E_{\tau}(AOIHO)$ ( $eV$ )	0	-13.50110	-13.13881	-13.6181
$E_{r}(n,ko)$ (eV)	-63.27075	-31.63539	-31.63532	-31.63247
$E_{\tau}(atom-atom, msp^3.\Lambda O)$ (eV)	-2.26759	-0.56690	-1.49608	0
$E_{r}(\omega)$ (eV)	-65.53833	-32.20226	-33.13145	-31.63537
$\omega \left(10^{15} \ rad \ l \ s\right)$	49.7272	26.4826	13.3984	44.1776
$E_{\kappa}$ (eV)	32.73133	17.43132	8.81907	29.07844
$\widetilde{\mathcal{E}}_{p}$ (eV)	-0.35806	-0.26130	-0.19465	-0.33749
$\overline{E}_{Kvib}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.12808 [19]	0.46311 [17-18]
$\vec{E}_{ m ure}$ (eV)	-0.25982	-0.08364	-0.13061	-0.10594
$E_{mag}$ (eV)	0.14803	0.14803	0.14803	0.11441
$E_{\tau}(cirum)$ $(eV)$	-49.54347	-32.28590	-33.26206	-31.74130
Entrat (c. AOIHO) (eV)	-14.63489	-14.63489	-14.63489	-13.6181
E (c, AOTHO) (eV)	0	-13.59844	0	-13.59844
$E_{\scriptscriptstyle D}(Gruup)$ (eV)	5.63881	3.90454	3.99228	4.41035

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			1	T	1		,		.]	;	Atom 2	>.	Alom I	F	26.	26.	20	and the sales of

# ANILNE

Aniline and methyl aniline have the formula  $C_6H_7N$  and  $C_7H_9N$ , respectively. They comprise the benzene and toluene molecules with one hydrogen atom replaced by an amino group corresponding to an  $NH_2$  functional group and a C-N functional group. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The C-C and  $CH_3$  functional groups of methyl anilines are equivalent to those of toluene given in the corresponding section.

The aryl amino  $(NH_2)$  functional group was solved using the procedure given in the Dihydrogen Nitride  $(NH_2)$  section. Using the results of Eqs. (13.245-13.368), the aryl amino 10 parameters in Eq. (15.51) are  $n_1 = 2$ ,  $C_1 = 0.75$ ,  $C_2 = 0.93613$  (Eqs. (13.248-13.249)),  $C_{1o} = 1.5$ , and  $c_1 = 0.75$ . In the determination of the hybridization factor  $c_2$  of Eq. (15.52) for the N-H-bond MO of aryl amines, the  $C2sp^3$  HO of the  $C-NH_2$ -bond MO has an energy of  $E(C,2sp^3) = -15.76868$  eV (Eq. (15.18) corresponding to s=2 in Eqs. (15.18-15.20), and the N AO has an energy of E(N) = -14.53414 eV. To meet the equipotential condition of the union of the N-H  $H_2$ -type-ellipsoidal-MO with the  $C2sp^3$  HO, the hybridization factor  $c_2$  given by Eq. (15.68) is

$$c_2(H \text{ to anline } N) = \frac{E(N)}{E(C, 2sp^3)} = \frac{-14.53414 \text{ eV}}{-15.76868 \text{ eV}} = 0.92171$$
 (15.151)

The bond between the amino and aromatic ring comprises a C-N functional group that is the same as that of  $2^{\circ}$  amines (methylene) except that the energies corresponding 20 to oscillation in the transition state are those of aniline. The group is solved using the same principles as those used to solve the primary and secondary-amine functional groups wherein the 2s and 2p AOs of each C hybridize to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and N AO to form a MO permits each participating hybridized orbital to decrease in radius and energy. The 25 hybridization is determined in a similar manner to that of the C-O group of phenol. In anilines, the aromatic  $C2sp^3$  HO has a hybridization factor of 0.85252 (Eq. (15.143)) with an initial energy of  $E(C,2sp^3) = -14.63489 \, eV$  (Eq. (15.25)) and the N AO has an energy

of  $E(N) = -14.53414 \, eV$ . To meet the equipotential condition of the union of the C-O  $H_2$ -type-ellipsoidal-MO with these orbitals, the hybridization factor  $c_2$  of Eq. (15.51) for the C-O-bond MO given by Eqs. (15.68) and (15.70) is

$$c_{2}(arylC2sp^{3}HO \text{ to } N) = \frac{E(N)}{E(C,2sp^{3})}c_{2}(arylC2sp^{3}HO)$$

$$= \frac{-14.53414 \text{ eV}}{-14.63489 \text{ eV}}(0.85252)$$

$$= 0.84665$$
(15.152)

- 5  $E_T(atom-atom, msp^3.AO)$  of the C-N-bond MO in Eq. (15.52) due to the charge donation from the C and N atoms to the MO is  $-1.13379 \, eV$  (Eq. (14.247)). It is based on the energy match between the  $NH_2$  group and the  $C2sp^3$  HO of the aryl group and is twice that of the aryl C-H group that it replaces.
- The symbols of the functional groups of aniline and methyl-substituted anilines are given in Table 15.243. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aniline and methyl-substituted anilines are given in Tables 15.244, 15.245, and 15.246, respectively. The total energy of each aniline and methyl-substituted aniline given in
- 15 Table 15.247 was calculated as the sum over the integer multiple of each  $E_{\scriptscriptstyle D}(c_{\scriptscriptstyle 1000p})$  of Table 15.246 corresponding to functional-group composition of the molecule. The bond angle parameters of aniline and methyl-substituted anilines determined using Eqs. (15.79-15.108) are given in Table 15.248.

20 Table 15.243. The symbols of functional groups of aniline and methyl-substituted anilines.

Functional Group	Group Symbol
CC (aromatic bond)	3" C=C
CH (aromatic)	CH (i)
Aryl C-N	C-N (a)
NH₂ group	NH <sub>2</sub>
$C_a - C_b$ (CH <sub>3</sub> to aromatic bond)	C-C (a)
CH₃ group	$C-H$ $(CH_3)$

	("A) H) (a) U-U	Graup Group	1,64920		1.04856	1	1,51904		1.524 1.11 (avg.) (toluene)	1	-	0.69673 0.63580	
HINCS BUT EXPERIMENTAL	Table 15.244. The geometrics congress congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress of the Congress	Group	90,750	1.20478	0.04124	0.74154	0.99627	1	0.998 (aniline)		0.81370	775653	
methyl-substituted an	(a) N= )	Group		1.81158		1.34595	1,42449		1.431 (anifine)		1,21254	24707	0.74231
has soldier to seeme	C1 13		1	190091		1.03299	7,460		1.084	(buend)	1 72265		0.04537
Manage Property of the second	cometrical condition	Ų.	Group	1 47'48	21.21.11	1,31468	97.05	04166	1.397 avg.	(byend)	O CASAO	0.00.0	FCC08 0
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Table 15.245. The MO to HO Intercept geometric Control of the Principle 15.245.	and in the control			ľ	-	Final Total				E(C25p)	 60	b-	s" ;	-	"〔
Bond	Atom	<sup>-1</sup> -√3	£ & £	F (S)	(eV) Band 4	Energy (2sp)	હ	્રે ઉ	Fina	Fine	 €	<u> </u>	C	<del>(f</del> )	(%)
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	]		0.35006	06995 0-	۰	-153,XX32K	0.91771	0 79597	.17.09134	-16.50248	74.43	s con			
(r-H (r.H)	. 1	-0,850.33	-d, nonus			01001	121100	0.88392	-15.39265	-15.2017R	20.83	101,11	43.13	1,20367	413311
C-H (C.H.)	٠,٠	-0.5FG9G	o	٥	3	-134.18239						20.05	67.69	0.47634	0.46500
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(C. = ) C.NH - H	2	W. W. C.						10110	Man 11	-16.9024R	47.83	15,18	41.01	1.36636	0,00,0
HW ( )	ن.	0.36600	-0.85035	-D #5UD5	c	-(53.11324	216.0	2,000			1	1			
					,		0.93014	0.68392	-15.39263		26.33	13.68	46,43	1,24859	0.09736
{ C; = } C; - NH;	≥	0452.a.	٥		=		·			1	†				
	]		,	-	•	.152.18259	0,91771	O.ER392	-15.39265	-15,20178	15.31	106.62	34.97	1,68207	62520
(Ca) Ch-Ch	·.	-4,300,90	,										;	577.6	100110
(x)	,	0077800	910340	-0.85035	e	-153.88328	1,51,71	0.79397	-17.09334	-14,90247	95,18	3	77.00	) Central	
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ر: الله الله الله الله الله الله الله الل	ئی · —	-0,45035	-0.11503.5	-0.56670	0	72888 221	17710	0,79397	recon.						
4	ປ"														
C=(H,C.)C.=C															

Table 15.246. The energy parameters (eV) of functional groups of aniline and methyl-substituted anilines.

Parameters	C=C Group	CH (i) Group	C-N (a) Group	NH <sub>2</sub> Group	C-C (a) Group	CH <sub>3</sub>
f <sub>1</sub>	0.75	1		Gloup	-	Group
n	2	1	1	2	1	3
$n_2$	0	0	0	0	0	2
$n_3$	0	0	0	1	0	0
$C_{\rm l}$	0.5	0.75	0.5	0.75	0.5	0.75
<i>C</i> <sub>2</sub>	0.85252	1	1	0.93613	1	1
<i>c</i> <sub>1</sub>	1	1	1	0.75	1	1
C <sub>2</sub>	0.85252	0.91771	0.84665	0.92171	0.91771	0.91771
<i>C</i> <sub>3</sub>	0	1	0	0	0	0
$C_4$	3	1	2	1	2	1
$c_5$	0	. 1	0	2	0	3
$C_{lo}$	0.5	0.75	0.5	1.5	0.5	0.75
C <sub>20</sub>	0.85252	1	1	1	1	1
V, (eV)	-101.12679	-37.10024	-32.76465	-78.97795	-29.95792	-107.32728
$V_{\rho}$ (eV)	20.69825	13.17125	10.10870	28.90735	9.47952	38.92728
T (eV)	34.31559	11.58941	9.04312	31.73641	7.27120	32.53914
$V_{m}(eV)$	-17.15779	-5.79470	-4.52156	-15.86820	-3.63560	-16.26957
E(логно) (eV)	0	-14.63489	-14.63489	-14.53414	-15.35946	-15.56407
$\Delta E_{H_2MO}(MOIHO)$ (eV)	0	-1.13379	-1.13379	0	-0.56690	0
$E_{f}(AOIHO)$ (eV)	0	-13.50110	-13.50110	-14.53414	-14.79257	-15.56407
E(n, хотно) (eV)	. 0	0	0	-14.53414	0	0
$E_{\gamma}(H_{2}MI)$ (eV)	-63.27075	-31.63539	-31.63549	-48.73654	-31.63537	-67.69451
$E_{\tau}(atom-atom, msp^3.AO)$ (eV)	-2.26759	-0.56690	-1.13379	0	-1.13379	0
$E_{\tau}(MO)$ (eV)	-65.53833	-32.20226	-32.76916	-48.73660	-32.76916	-67.69450
$\omega \left(10^{15} \ rad \ / \ s\right)$	49.7272	26.4826	11.9890	68.9812	16.2731	24.9286
$E_{\kappa}$ (eV)	32.73133	17.43132	7.89138	45.40465	10.71127	16.40846
$\bar{E}_{D}$ (eV)	-0.35806	-0.26130	-0.18211	-0.42172	-0.21217	-0.25352
$ar{E}_{ extit{KVL}}\left( eV ight)$	0.19649 [49]	0.35532 Eq. (13.458)	0.15498 [54]	0.40929 [22]	0.14940 [53]	0.35532 (Eq. (13.458))
$\widetilde{E}_{aw}(eV)$	-0.25982	-0.08364	-0.10462	-0.21708	-0.13747	-0.22757
$E_{min}(eV)$	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\tau}(Group)$ (eV)	-49.54347	-32.28590	-32.87379	-49.17075	-32.90663	-67.92207
E <sub>lantol</sub> (c, AOIHO) (eV)	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489
Einthal (c, AOIHO) (eV)	0	-13.59844	0	-13.59844	0	-13.59844
$E_D(Group)$ $(eV)$	5.63881	3.90454	3.60401	7.43973	3.63685	12.49186

rental values [2].	
to the expens	Relative
ole 15.246 compared	Total Bond Energy
the energies of Lab	Calculated Total Bond
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				•		(a) (b) (b)	120.19 [30-52] (benzene)	119.91 (benzene)	113.89 113.9 (aniline)	77.10
						ø ©				
						9 (		120.19		
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						E, (eV)	-1,85836		0	-
Rulative Error	-0.00093	0.00025	0.00050	0,00040		ፕ	0.79232		1.06823	10101
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Total Band Factor (aV)	FA.4337	76,62343	76.624	76,62345	om,msp'.AO).	Alans 2	0,79232		-	0 86284
CH,	a	-	_	_	: E <sub>r</sub> (atom – at	C; Alees 1	a.79232		0,93613 Eq.(13,241))	0.84665 0.86284
C-C (a) Group	٥		-	-	values [1]. E, is	Aton 2 Hybridization Designation (Table 15.3.A)	z		Ι	•
WH.	] .  -	-		-	l experimenta	Eronana Asmit	.17.17218		'n	19 05055
C - N (a) Group		_	_	-	brituted anilines and experimental values [1]. $E_{ m r}$ is $E_{ m r}(anom-anom,mrp^2,AO)$	Atom I Hybridization Designation (Table 15.3.A)	7.		z	z
(1) (1)	_	<b>-</b>	7		nethyl-subst	Ermanna Atom I	-17,1721X		1 RKZGK 3.1559 -14,53414	-14.53414
ť					ine and i	2c' Torrand Atoms (a,)	4 5585		3,1559	4 0332
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					de parsınd	2¢' Ima I (a,)	2.62936		I.XXZ6H	KAZKKI
Name	Aniline	2-methylaniling	3-muthytamiline	4-methylaniline	Table 15.248. The bond angle parameters of anitine and methyl-sul	Aktus of Angle	ZCCX*	Δ' ''H (arounatic)	CHNH.	CHNL.
Formula	N,H,O	マデン	C,1,2	CHIN	Table 15					

## ARYL NITRO COMPOUNDS

Aryl nitro compounds have a hydrogen of an aryl group replaced by a nitro corresponding to an  $NO_2$  functional group and a C-N functional group. Examples include nitrobenzene, nitrophenol, and nitroanilne with formulas  $C_6H_5NO_2$ ,  $C_6H_5NO_3$ , and  $C_6H_6N_2O_2$ , respectively. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The OH and C-O functional groups of nitrophenols are the same as those of phenol given in the corresponding section. The  $NH_2$  and C-N functional groups of nitroanilines are the same as those of aniline given in the corresponding section. The differences between the total bond on the energies of the nitroanilines given in Table 15.252 are due to differences in the  $E_{ax}$  term. For simplicity and since the differences are small, the  $E_{ax}$  terms for nitroanilines were taken as the same.

The  $NO_2$  group is the same as that given in the Nitroalkanes section. The bond between the nitro and aromatic ring comprises a C-N functional group that is the same as 15 that of nitroalkanes given in the corresponding section except that  $E_T(atom-atom,msp^3.AO)$  is -0.72457~eV, one half of that of the C-N-bond MO of nitroalkanes and equivalent to that of methyl (Eq. (14.151)) in order to maintain the independence and aromaticity of the benzene functional group. In addition, the energy terms due to oscillation in the transition state correspond to those of an aryl nitro compound.

The symbols of the functional groups of aryl nitro compounds are given in Table 15.249. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of aryl nitro compounds are given in Tables 15.250, 15.251, and 15.252, respectively. The total energy of each aryl nitro compound given in Table 15.253 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.252 corresponding to functional-group composition of the molecule. For each set of unpaired electrons created by bond breakage, the  $C2sp^3$  HO magnetic energy  $E_{mag}$  that is subtracted from the weighted sum of the  $E_D(Group)$  (eV) values based on composition is given by Eq. (15.58). The bond angle parameters of aryl nitro compounds determined using Eqs. (15.79-15.108) are given in Table 15.254.

Taryl mito compound: Group Symbol	36	CH (i)	C - N (a)	C-N (b)	C-O (a)	NO,	NH.	HO	
Table 15.249. The symbols of functional groups of aryl mitto compounds.  Group Symbol	runctional Group	CC (aromatic bond)	CH (aromatic)	Aryl C-N (aniline)	Aryl C-N (nitro)	Aryl C-O	NO <sub>2</sub> group	NH, group	Off prolin

	HO	Group	1 26430		0.91808			0.971651		0.956	(phenol)		0.86925	0.72615		
	NH	Group	1 24470	1.24420	0 94134	24.60		0.99627		0 998	(aniline)		0.81370	257560	0.00.0	
Ξ		100 J	Group	1.33221	10731	1.12461.1		1.22157		1.224	(nitromethane	,	0.66526		0.86639	
acrefiere 1 - i	hand narameters of aryl nitro compounds and experimental values [1]	C-O (a)	Cronb	1.68220		1.29700		1.37268			1.364 (phenol)	,	1 07126	1.0.1	0.77101	
	mpounds and ex	C-N (b)	Group	1 07704	1.711.71	1 40639		1 49846	1.4004.1				01000	1.39079	0 71104	0:/1101
	s of aryl nitro col	C-N (a)	Group	0,110	1.81158	1 24505	1.34373		1.42449	-	1.431	(annue)		1.21254	20000	0.74297
	I hand parameter	CH (c)	Group	•	1.60061		1.03299		1.09327		1.084	(phenol)		1 22265		0.64537
	Tr monthing	Table 15.250. The geometrical	ر ر=ر	Croup	1.47348		1.31468		1,39140		1.397 avg.	(lohenol)	,	0 66640	0.00040	0.89223
On Broup		Table 15.250.	Parameter		(0)0	(0)	$c'(a_n)$	Bond	Length	2c' (Å)	Exp. Bond	11911	\(\varphi\)		p,c (a0)	

1		l													
	Ytom 	(eV) Bond )	Er (eV) Band 2	(eV)	(eV)	Final Total Energy	) (e)	13.0	(eV)	E(C242)	.0 3	6-3	63	d,	3
(-H (CH)	1				b buog	\$ S	: 	(8)	Find	E E	= 	= _	E 	(°	<u>ે</u>
( - x )	ان	-0.83035	-0.45035	-0.36690	•	-153.88327	0,91771	0.79597	L7 09 71	16 00 14					
(C,=),C,O-H	9	-0.74XD4	•	С	c		1.0000	0 17763	1	200	7	105.58	2	1.24678	0,21379
HO-") (" - OH	ن	-0.74804	-0 \$3035	-0.85035	6	11.000.00			· ·		113.79	64.21	64.82	0.53799	0.38009
HO- J (")	,				•	76MIN'1011	0.01771	0.78762	-17.27448	-17.08362	100.00	80.00	46.39	1.16026	0.13674
(, ')		-0.74H04	c	0	0		1,00000	0.87363	15.57379		106.51	73.49	51.43	1,04871	0.24829
W. ( a )	U <sup>t</sup>	-0.74804	-0.X5033	-0.85033	٥	-154.06442	17716.0	0.78762	-17.27448	-17.08362	133.88	46.12	58.55	0.76370	200
('={H,N}C'=C' '*	ن:													Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Control of the Contro	U. ACASON
(=(H)C, ), C,OH	<i>ਦ</i> ਦ	-0.85035	-0.85035	0.56690	۰	-153.KR327	0.91771	0,79397	-17.09334	-16.90248	134.24	45 76	8	***************************************	
C=(H,C,)C,=C	ن•													COCCUT.	433333
$C_{s}=$	×	-0.56690	o	0			74025-0	Social A							
(C, ") C, ~ NH;	ن	-0,566pp	-0.83033	-0.85035	•	100		7,000,0	-13.3926S		121,74	58.26	67.49	0.4763.4	0.46.500
C. # C NH.	3	D 66610			•	HJCHB.CCI.	0.91771	7080Y.0	LCE60,71.	-16,90248	11.49	15.19	41.01	1.36696	0.02101
			-	•	6		0.93084	0.14392	-15.39265		26,32	#3.6#	46,43	1,24859	0.00736
( * ) ( * ) ( * )	ر.'	-0.36690	5	c	c	-152.18259	0.91771	0.88392	-15.39263	-15.20178	73.38	106.67	6075		
$\left(C\mathbf{n}\right)C_{r}-C_{s}H_{s}$	ŗ,	-0.36690	-0.85035	-0,K\$033	0	-153 RH328	0.91771	0.79597	-17.09334	-16 ansa7	1			I.nsku/	0.25279
0 = (O) = O	0	-0.9294x	•	l		1					97.15	¥	28.27	1,11430	0.37901
(c)	2	A1020.D	4192918	0.34229	С			O.K6359	-15.75493		135.25	44.75	66.05	0.54089	0.61333
(C=) C, - NO;	ن'	-0.34229	-0.113035	-0.85655	-		Tance of	0.79816	-17.04640		132.36	3,75	62.44	0.61640	0.53781
(C=), C, -NO,	2	-0.7271R	40.07918	mest o	,	1000000	1111671	0.#0361	.16.RRK73	-16 697%	72.49	107.51	33.53	1,64875	0.24236
(O,N)(',=('	1	0.36229	25024.0		•		0.93084	0.79x16	-17,04640		71.53	103.47	32.9x	1,65923	0.252M
			ecacu's.	-0.85035	•	153.67867	177160	0 x0561	-IG,RRR73	-16 697RG	17.00	1			

Table 15.251. The MO to HO intercept geometrical bond parameters of aryl nitro compounds.  $E_t$  is  $E_t$  (atom – atom, map  $^*$  AO).

Table 15.252. The energy parameters (eV) of functional groups of arvl nitro compounds.

Table 15.252. The energy parameters	C=C	CH (i)	C - N (a)	C-N (b)	C-O (a)	NO,	NH,	ОН
	Group	Group	Group	Group	Group	Group	Group	Group
<i>f</i> <sub>1</sub>	0.75	1						
n <sub>i</sub>	2	11	1	. 1	1	2	2	1
n <sub>2</sub>	0	0	0	0	0	0	0	0
<i>n</i> ,	0	0	0	0	0	0	1	0
C <sub>i</sub>	0.5	0.75	0.5	0.5	0.5	0.5	0.75	0.75
C,	0.85252	1 1 .	1	1	1	1	0.93613	i
9	I	1	1	1	1	1	0.75	0.75
<i>c</i> <sub>3</sub>	0.85252	0.91771	0.84665	0.91140	0.79329	0.85987	0.92171	1
63	0	1	0	0	0	0	0	1
c,	3	1	2	2	2	4	1	1
<i>c</i> <sub>3</sub>	0	1	0	0	0	0	2	1
Cin	0.5	0.75	0.5	0.5	0.5	0.5	1.5	0.75
C <sub>2</sub> ,	0.85252	1	1	1	1	1	1	1
V. (eV)	-101.12679	-37.10024	-32.76465	-31.36351	-34.04658	-106.90919	-78.97795	-40.92709
V, (eV)	20.69825	13.17125	10.10870	9.67426	10.49024	23.57588	28.90735	14.81988
T (eV)	34.31559	11.58941	9.04312	7.92833	10.11966	40.12475	31.73641	16.18567
V <sub>m</sub> (eV)	-17.15779	-5.79470	-4.52156	-3.96416	-5.05983	-20.06238	-15.86820	-8.09284
Ε(λυτήο) (eV)	0	-14.63489	-14.63489	-14.63489	-14.63489	0	-14.53414	-13.6181
$\Delta E_{H_1 \downarrow JO}(AOINO)$ (eV)	0	-1.13379	-1.13379	-0.72457	-1.49608	0	0	0
$E_{r}(\text{-nino})$ (eV)	0	-13.50110	-13.50110	-13.91032	-13.13881	. 0	-14.53414	-13.6181
E(», могно) (eV)	0	0	0	0	. 0	0	-14.53414	0
$E_{T}(H_{z}\omega)$ (eV)	-63.27075	-31.63539	-31.63549	-31.63540	-31.63532	-63.27093	-48.73654	-31.63247
$E_{r}(atom-atom, msp^{3}.AO)$ (eV)	-2.26759	-0.56690	-1.13379	-0.72457	-1.49608	-3.71673	0	0
$E_{\gamma}(\omega)$ (eV)	-65.53833	-32.20226	-32.76916	-32.35994	-33.13145	-66.98746	-48.73660	-31.63537
ω (10 <sup>15</sup> rad / s)	49.7272	26.4826	11.9890	17.8228	13.3984	19.0113	68.9812	44,1776
$E_{\kappa}$ (eV)	32,73133	17.43132	7.89138	11.73128	8.81907	12.51354	45.40465	29.07844
$\bar{E}_{\nu}$ (eV)	-0.35806	-0.26130	-0.18211	-0.21927	-0.19465	-0.23440	-0.42172	-0.33749
$ar{E}_{ m Krib}$ (eV)	0.19649	0.35532	0.15498	0.10539	0.12808	0.19342	0.40929	0.46311
$\bar{E}_{ac}(eV)$	[49] -0.25982	Eq. (13.458) -0.08364	[54] -0.10462	[45]	[19]	[45]	[22]	[17-18]
$E_{\text{max}}(eV)$	0.14803	0.14803		-0.16658	-0.13061	-0.13769	0.21708	-0.10594
$E_{\tau}(Group)(eV)$	-49.54347		0.14803	0.14803	0.14803	0.11441	0.14803	0.11441
$E_{hilled}(\epsilon, AUIRO)(eV)$		-32.28590	-32.87379	-32.52652	-33.26206	-67.26284	-49.17075	-31.74130
$E_{tribut}(c, 30110)$ (eV)	-14.63489	-14:63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414	13.6181
$E_{t_i t_i t_i t_i} (\epsilon, 3010) (eV)$	5.63881	-13.59844	0	0	0	0	-13.59844	-13.59844
D (Comp) (Cr)	18860.0	3.90454	3.60401	3.25674	3.99228	8.72329	7 43973	4 41035

Table 15.253. The total bond energies of any nitro compounds calculated using the functional group composition and the energies of Table 15.252 compared to the experimental values [2]. The magnetic energy $E_{meg}$ that is subtracted from the weighted sum of the $E_{b}$ (60mm) (e	values based on composition is given by (15.58).  Relaine  N. O.H. G. Tanil Bood Engine

							ſ			Γ	-										1
								ė.	Đ	120 (50-52)	(benzene)	120 (50-52)	125.2 [54]	(ni:robenzene) 1253	(F2) 5 61 1	(nitrobenzene)	0.601	To a second	(aniline)		
	Relative	Þ	9049	0.00070	2003			٠ ا	c C		120.19	16.611	1	126.52		118,82	109.84		113.89	30 00.	· come
								φ,	·S				T	-							
	Experimental	No carento	77	72,424	2			φ,	Œ	T		120.19									
	E	200	3 :	143	2.2			θ,	C											L	
	Calculand	Total Bond Energy (eV)	65.18754	72.47476	72,47476			Ħ	· (§		-1.85836			-1.44015		-1.65376	6		0		0
		<b>1</b>	-	n 0				,	, .		0.79132			0.81549		0.81570	12210		1.06823		0000071
								,	r		-			_		_		27.73	67.0		27.
	100	Group	0	-0	00				ŗ.					_		_		-	-		_
	NE	Group	0	٥-				ز			-			_		-		C	_		87.9
		- c						,	C <sub>1</sub>		0,79232			0.81549		0.85395 (Eq.	(18,114)	0.91771	_	0.14665	(E
	1	֓֞֞֞֞֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓֓	-	~ ~			(Or a)		Abr 1		0,79232			0.81549		0.77945		-	0,93613 Eq.	(13.24R) 0.14665	(Eq.
		C + O (a)		> — c			experimental values [1]. E. is E. (atom - atom, msp. AO)	A tom 2	Hytridization Designation	(Table 15.3.A)	75			72		0		_	×		z
		(a) د ارد ارد	1	- 14 -			cs [1]. E. is B		Atom3		1177171			-16.68411	 e*	-13,61806		-14,82375	Ξ		-14.53414
		(a) N - U	dnon	<b>.</b>			cnerimental valu		Atom I Hybridization Designation	(Table 153.A)	7			-	;	₽		-	2		6
		CH (i)	1	v 4	44				Franks Atom i		1	41771711-		11789'91-	c, 	1745169		-14.12575	-1453414		15.95955
		ວ					2000		2c° Terminal Alberta	3	+	arr,				1		3.6515	31580		3.9833
aryı mino	15.58).	ر د ا	3	~ ·	~ ·c	٤	in bear	101 My 11	, 5c.	 }	┿	262936		-	2,30843		⊣	1,83616	_	+	1,xB26B
energies of	given by (							parameter	26. Bod.		+	2.62936		_	2,304.5	+	77.17.7	2 59399			2.69190
Table 15,253. The folal bond energies of any mile compounds the	values based on composition is given by (15.58).	Nama N		Nitrobanzano 2,4-dinitrophesol	2-nitromiline 3-nitromiline	4-aitrosniline		Table 15,254. The bond angle parameters of any titue compounds and	Akores of Aegie		,,,,,,,	, 	ACCH.	archinauc)	ZD,NO.		ZCNO	HO:37		דוואנו	HN .J/
Table 15.25	values based	4		CH,NO,	000 22 11 11 11 11	CHANO		Table 15,2;	av 	_					-						

#### BENZOIC ACID COMPOUNDS

Benzoic acid compounds have a hydrogen of an aryl group replaced by a carboxylic acid group corresponding to an C-C(O)-OH moiety that comprises C=O and OH functional groups that are the same as those of carboxylic acids given in the corresponding section. The single bond of aryl carbon to the carbonyl carbon atom, C-C(O), is also a functional group. This group is also equivalent to the same group of carboxylic acids except that  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom,msp^3.AO)$  in Eq. (15.52) are both -1.29147~eV which is a linear combination of  $\frac{-1.13379~eV}{2}$ ,  $E_T(atom-atom,msp^3.AO)$  of the C-H group that the C-C(O) group replaces, and that of an independent  $C2sp^3$  HO, -0.72457~eV (Eq. (14.151)).

Examples include benzoic acid, chlorobenzoic acid, and aniline carboxylic acid with formulas  $C_7H_6O_2$ ,  $C_7H_5O_2Cl$ , and  $C_7H_7NO_2$ , respectively. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The  $NH_2$  and C-N functional groups of aniline carboxylic acids are the same as those of aniline given in the corresponding section. The C-Cl functional group of 2-chlorobenzoic acids corresponding to meta substitution is equivalent to that of chlorobenzene given in the corresponding section. The C-Cl functional group of 3 or 4-chlorobenzoic acids corresponding to ortho and para substitution is also equivalent to that of 20 chlorobenzene, except that  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom,msp^3.AO)$  in Eq. (15.52) are both  $-0.92918 \, eV$  (Eq. (14.513)) since each of these positions can form a resonance structure with the carboxylic acid group which is permissive of greater charge donation from the  $C2sp^3$  HO.

The symbols of the functional groups of benzoic acid compounds are given in Table 15.255. The corresponding designations of benzoic acid is shown in Figure 64. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of benzoic acid compounds are given in Tables 15.256, 15.257, and 15.258, respectively. The total energy of each benzoic acid compound given in Table 15.259 was calculated as the sum over the integer multiple of

each  $E_D(Group)$  of Table 15.258 corresponding to functional-group composition of the molecule. The bond angle parameters of benzoic acid compounds determined using Eqs. (15.79-15.108) are given in Table 15.260.

5 Table 15.255. The symbols of functional groups of benzoic acid compounds.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH (i)
C-C(O)	C-C(O)
C=O (aryl carboxylic acid)	C = O
(O)C-O	C-O
OH group	OH
Cl-C (Cl to aromatic bond of 2-chlorobenzoic acid)	C-Cl (i)
Cl-C (Cl to aromatic bond of 3 or 4-chlorobenzoic acid)	C-Cl (ii)
Aryl C-N (aniline)	C-N
NH <sub>2</sub> group	NH <sub>2</sub>

	ſ		7		Ţ	_	Γ	_	Τ		7	-	
		יאמי	Group	1.24428		0.94134	10,000	0.39627	0,998	(anihne)		0.81370	
	7	ع د ع د	diam	1.81158		1.34595	07727	C4474.1	1.431	(miline)		1,21254	
	(E) (C) (E)	Gran	2000	4.19338	20077	1,04243	1,73827		1.737	(disconstant)		1.45403	
	C-C/ (i)	Group	2 20.700	45077	1 64703	70/101	1.74397		1.737	(2022)	. 4000	10001	0-3750
	HO	Group	1,26430	20.00	0.91808		0.971651		0.972 (formio acid)		20380	C#5000	0 77614
	0-0	Group	1.73490		1.31716		1.39402		1.393 (inethyl formate)		1.12915		0.75921
entel values [3]	0=3	Стопр	1,29907		1.13977		1,20628		1.214 (acetic acid)		0.62331	100000	0.01/2/
compounds and experimental values []	(0)2-2	deep	11.95111		1.39682		1.47833		1.48 [55] (benzoic scid)		1.36225	0 7/501	2011
The state of the profite in the parameters of pensole acid comp	() HD	diors	1.60061	40000	66750.1		1.09327		1.101 (benzene)		1.22265	0.64537	
THE POINTERNAMI DONG DE	ں ا ان را	Group	1.47348	SYPIE	2010		1.39140		1.399 (benzene)	0.555.0	0.00340	0.89223	
	Parameter		a (a°)	c, (a)		Bond Length	2c' (A)	Exp. Bond	Egg Egg	10/04	[v <sub>n</sub> ]	,	

Table 15.257. The MO to HO intercept geometrical band parameters of benzoic soid compounds.	metrical bon	d parameters of t	renzoic acid com	pounds. E, is	E, is E, (atom - atom, nisp'. AO)	", misp' .AO).									
Bond	Aton	1.21	F.	T.	E,	Final Total	.1:	1	Erms (Cap')	$E(C2sp^3)$	.0	6	e. (	<sup>1</sup> p	~"〔
		(eV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	(S & )	(a.)	(a,)	Final	(eV) Final	Ē.	E	<b>E</b>	(%)	(%)
C-H (C,H)	ű	-0.85035	-0.R5tG5	-0.36690	٥	-153.88327	0.91771	0,79597	-17.09334	-16.90248	74.42	105.58	38.84	124678	0.21379
C=HC,=C C=(HXX;)C,=C(H), C=(C)C,=C,(H) C=(HX)C=C(H)	ಕಟ್ಟಿಕ	-0, K5035	-0.85035	06995'0'	0	-153.88327	0.91771	G.70597	-17.09334	-16.9248	134.24	45.76	58,92	Q.75935	0.55533
$C_{r} = C_{r}(0)O - H$	0	-0,9291K	-	c	o		1.00000	0.86359	-15.75493		115.00	164.91	64.12	28185,0	0.36625
(C, "), C.(O) -OH	2	-0.9291K		0	0		1,0000	0.84359	-15,75493		25.101	78.68	48.58	1.14763	0,16950
(C, =) C.(0) - OH	Ų.	.0.9201R	99675.1.	-0,64574	0	-154.54007	0.91771	0.76652	-17,75013	-17.55927	11.8%	841.89	42.6R	1,27551	0,04163
$\left(C, \stackrel{\square}{\leftarrow}\right) C_{\sigma}(OH) = O$	0	1.349Jf	0	•	c		1,0000	0.84115	-16.17521		137.27	473	1631	0.52153	0.61784
$\left(C_{\mu}^{2}\right)_{j}C_{\mu}(OH)=0$	U.	1.34946	-0,64374	4.92918		-154.54007	17716.0	0.74452	-17,75013	-17.55927	134.03	43.77	62.14	0.60099	8/252.0
C',=(H/XX_)C,=C, (C, bound to H, C', or NH,)	ئ	-0,64574	-0.85035	\$£0\$X:0-	0	5153.96212	12216.0	0.79232	-17,17218	-16.98132	134.09	45.91	58.79	0.76344	0.53124
(C= ) (= )	٦	.0.3G27	9	0	c		1.05158	0.895#2	15.18804		12,52	97.08	17.22	1,75824	0.11042
D~ () (=.)	ڻ	-0.3(229	-0,85035	-0.85035	c	.153.57 <b>2</b> 67	11216.0	0 80361	-16 88873	-16.697RG	73.32	19701	29'10	11678,1	0.23129
C, =(C)X', =(', (', bound to H or C!)	Ů,	-0.36229	-0.85035	0.85035	o	יואנאנט.	0.91771	0 80561	-16.88873	-16.697BK	134.63	45.35	59.47	0,74754	0.56614
(C, ") C,NH - H	×	-0.56490	c	٥	o		0.93014	0.11392	-13.39265		121.74	51.26	67.49	0.47634	0.46300
$\left(C, \frac{\lambda}{\pi}\right)_{C_{\mu}} - NH_{2}$	Ů.	-0.56690	-0, R 5035	0.85035	0	-153,R8328	0.91771	0.79397	-17.09334	-16.90248	ER.49	91,51	41.01	1,36696	0 02101
$\left(C_{s}^{n}\right)C_{s}-NH_{s}$	~	0.56690		0	0		0,93084	0.81392	-15.39265		96.32	13.61	66,43	1,24859	90.09736
C=(H,N)C,=C	ŗ.	-0.85035	-0.85035	06275-0-	0	-153,883,7	17116.0	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0,75935	0.55533

Parameters	, u	C.H. (i)	(O)-U	0=0	2 E	Sound Thousand	C-G (5)	C-C/ (ii)	C-N Graup	, HH,
1/	0.75	-								
u'	2	-	-	2	-	,	1	1	-	2
u,	0	٥	0	0	0	0	0	0	0	0
li,	0	0	٥	٥	0	0	0	0	0	
	0.5	0,75	20	0.5	0.5	0.75	0.5	0.5	0.5	0.75
	0.85252	_	_	1	1	1	0.81317	0.81317	-	0.93613
ប	-	_	-	-	-	0.75	-	-	1	0.75
ر.	0.85252	0.91771	0.91771	0.85395	0.85395	1	ı	-	0.84665	0.92171
<sup>1</sup> 3	c	-	0	2	0	_	0	0	0	0
ប		_	2	4	2	1	2	2	2	-
6,5	0	1	0	0	0	1	0	0	0	2
ر.	0.5	0.75	5.0	0,5	0.5	0,75	0.5	5.0	0.5	1.5
ر^	0.85252	_	-	-		1	0.81317	0.81317	1	-
V, (cV) ·	-101.12679	-37.10024	-32.15216	-111,25473	-35.08488	-40.92709	-31,85648	-32,14474	-32.76465	-78.97795
(cV) "V	20.69825	13,17125	9.74055	23.87467	10,32968	14,81988	8,25686	8.28594	10.10870	28.90735
(A) J	34,31559	11.58941	8.23945	42.82081	10,11150	16.18567	7.21391	7.32700	9,04312	31,73641
(AD) "A	-17,15779	-5.79470	4.11973	-21.41040	-5.05575	-8,09284	-3.60695	-3.66350	4.52156	-15.86820
E(m no) (cV)	0	-14.63489	-14,63489	0	-14.63489	-13,6181	-14.63489	-14.63489	-14.63489	-14.53414
(72) [m m] (ch)	o	-1.13379	-1.29147	-2,69893	-2.69893	0	-2.99216	-2.99216	-1.13379	0
F. (10 w) (cV)	0	-13,50110	-13,34342	2.69893	-11,93596	1819.51-	-11.64273	-[1.64273	-13.50110	-14,53414
F(4, on to) (uV)	0	0	0	0	0	0	0	0	0	-14.53414
Eplusians (eV)	-63.27075	-31.63539	-31.63530	-63.27074	-31,63541	-31,63247	-31,63539	-31.65542	-31.63549	-48.73654
$E_{\tau}(atom - atom, msp^2, AO)$ (or)	-2.26759	-0.56690	.1.29147	-2.69893	-1.85836	C	-0.72457	-0.92918	-1.13379	0
E, (sm) (cV)	-65,53833	-32.202.26	-32,92684	-65.96966	-33,49373	15559,15-	-32,35994	-32,36455	-32,76916	-48.73660
w (101: rod/s)	49.7272	26.4826	10,7262	59,4034	24.3637	944.1776	8.03459	8.11389	11.9890	68.9812
6, (eV)	32.73133	17.43132	7,06019	39,10034	16.03660	29.07844	5.28851	5.34070	7.89138	45.40465
E, (eV)	-0.35806	-0.26130	-0.17309	-0.40804	-0.26535	-0.33749	-0.14722	-0.14888	-0.18211	-0.42172
Ex+ (eV)	0.19649	0.35532 Eq. (13.458)	(62) (29)	6,21077	0.14010	0.46311 [17-18]	0.08059 [12]	0.08059	0.15498	0.40929
E. (eV)	-0.25982	-0.08364	*0.12058	-0.30266	-0.19530	-0.10594	-0.10693	-0.10859	-0.10462	-0.21708
Em (aV)	0.14803	0.14803	0.14803	0.11441	0.14803	0.11441	0.14803	0.14803	0,14803	0.14803
Er (rang) (cV)	49.54347	-32.28590	-33.04742	-66.57498	-33,68903	-31.74130	-32.46687	-52.67314	-32,87379	-49.17075
E (0, .m m) (eV)	-14,63489	-14,63489	-14.63489	-14.63489	-14,63489	-13.6181	-14.63489	-14.63489	-14.63489	-14.53414
E (4. 40.10) (4V)	0	-13.59844	0	0	٥	-13.59844	0	0	0	-13,59844
$E_{\mu}(com)(aV)$	5.63881	3.90454	3.77764	7.80660	4.41925	4.41035	3.19709	3,40336	3.60401	7,43973

								100		STALL 16 24	St. commune	the creek	inental va	thes [2].						
Table 15.259.	Table 15.259. The total bend energies of benzoic acid connounds cal	energies o	f benzoic a	cid compc	nuds calcul	ated using the fun	ichianal group	culated using the functional group composition and the criciples of 1806 15.230 compount in we experiment and conference of the Carlo Compount in Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carlo Carl	ne mergies	)-U	0-0.0	(i) (i) -0	ن	×	NH,	Calculated Total Bond	1	Experimental Total Bond Fronts	Refativo	
Formula	Name		ပ ပ		3 7	ניינים		C C C	Group	5		Grand	Ğ	Group	Group	Encry (c	-	(0)		
			Cronp	١	dno	dnon	danio	200	-	0				-	0	73,76938		73.762	G00000°	
CHO	Barroic acid		9 .		<b>.</b>					_	_	۵	_	_	-	13.061		73.082		
, F, CIO,	2-chlorobenzbic scid	<b>.</b>	٠.		. ,		. ~		_	,	6	_	-	c	,	73.26K		077		
£,00	-chloropenzbie acid	9.	•		, ,				-	•		-	_		٥.	10.00		1000		
CHICO	4-chigaroscrizzac edic	9 .	. •		, 4		-	_	-			0				CHUC DS		11.01		
CHING	Andine-3-carbonylic send	lie send				<b>-</b> -	<b>~</b>					<b>5</b> C				80,20837		80.949	0.00030	
SHING	Antling 4-carboxvile scid	Jie scid							10, 7				!							
Table 15.260.	Table 15.260. The bond angle parameters of benzoic acid compounds	e paramete	rs of benze	ric acid co	anpounds an	d experimental vi	ames [1]. E.	and experimental values [1]. Er 13 Er (origin - digni, nich . A.)	I' next dring			-	-	-	-	-	+	Cala		
Norw of Angl	e Angle	٤٤	24.7 Red 2	Ternical	S. Carlotte	Alom 1 Hybridization	1	Atom 2 Hybrid zation	, F	ر <u>ا</u>	 ن	<u>.</u> "	v	 V'	4 §	D, Œ	5° ©		e -	
		(0)				Designation	i	Designation								=	-			- }
לננג	ز	Ames,	3,693,6	-	.17.67208	X X	-17.17218	7	0,70131	0 79232	-	-	-	0.79232	-1.MS836			130.19	(20)50-51 (benzene)	
(aromatic)	laric)										-	+	-	-		-	120.19	19.91	_	
/ammatic)	nutic)				_					+		+	+	+		1	+		1	
HO.D	17	163.03	1,83616	3 6-605	-14.82575	-	-14 82575	_	<u>.</u>	0.91771	57.0	-	23	0.91771	0	+	+	100	1	
) V	C.C.O.	2.82796	227054	14771	17,17214	×	-13.61 xx	0	0.70232	0,8395 (Eq.				CIEZA)3	-1.63376			121.56	122 (35) (Donazie acid)	اء
	11.00	A(17.0x c	2,634	4.6090	-16.40067	2	.13,61806	0	0.KZ959	0.RS733 (Pt.	-	-	-	0,144 77	-1.63376		-	117.43	118 (55) (berzoie acid)	-
i					16.17521		.15,75493	,	11171	((5114))	1-	<del> </del>	•	A KSZSY	-1,44913		+	126.03	122 (55)	
07	70°C07	117954	1043	4,3878	\$,	č	ď	`	CHERT	U.M.D.S.	-	-	1	1		1	$\dagger$	+	1	
*						:		;	į	5,502.0				25700	1.83836			120.19		ပု 😧 ၊
i gag	(aromatic)	261936	2.42936	7.5385	XIZC.FI-	<b>3</b>	# 170.34c	<b>.</b>			•		·						chlorobenzene) (20150-52) (benzene)	ĵ.
77	1.1.17 H.1.17																120.19	119.91		
*5	CHNH	1. B.N.Zr.st	1,4826K	3.1589	-14.53414	z	2	x	0,93613 Eq.	_	_	-	0.75	1,00,023	0			(I.E.)	(aniliere)	- 1
), A	HK. YH	2,69190	2.60190 1.88208 3.9M33	3.9903	-15.05955	•	MEC NI.	z	0.84665 (Eq.	0.84665 (Eq.	67.9	-	0,73	1.00000	0			170.05		

## **ANISOLE**

Anisole has the formula  $C_7H_8O$  and comprises the phenol molecule with the hydroxyl hydrogen atom replaced by the moiety  $-O-CH_3$  to form an ether comprising aromatic and methyl functional groups as well as two types of C-O functional groups, one 5 for aryl carbon to oxygen and one for methyl carbon to oxygen. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in Aromatic and Heterocyclic Compounds section. The  $CH_3$  and methyl C-O functional groups are the same as those of the corresponding ether groups given in the corresponding section.

The C-O functional group comprising the bond between the ether oxygen and aromatic ring is equivalent to that of the methyl ether C-O functional group except that  $\Delta E_{H_2MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom,msp^3.AO)$  in Eq. (15.52) are both -1.13379~eV (Eq. (14.247)).  $E_T(atom-atom,msp^3.AO)$  is based on the energy match between the  $OCH_3$  group and the  $C2sp^3$  HO of the aryl group and is twice that of the aryl C-H group that it replaces.

The symbols of the functional groups of anisole are given in Table 15.261. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of anisole are given in Tables 15.262, 15.263, and 15.264, respectively. The total energy of anisole given in Table 15.265 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.264 corresponding to functional-group composition of the molecule. The bond angle parameters of anisole determined using Eqs. (15.79-15.108) are given in Table 15.266.

Table 15.261. The symbols of functional groups of anisole.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	· CH (i)
Aryl C-O	C-O (a)
Methyl C-O	C-O (b)
CH, group	$C-H$ $(CH_3)$

58.98

0.91771

٠,٠

0.16921

38.84 42.40 46.10

105.58 101.15 84.02

74.42 78.85 95.98

(g) "g

(o) q

°.⊙

θ<sub>1</sub> (C)

6 E

0 04975

41.36 43.36

93.00

91.59

93.18

I	he geometrical bo	Table 15.262. The geometrical bond parameters of anisole and experimental values [1]	nisole and experir	nental values [1].	
Parameter	ں ا ا	0 %	( - O (a)	(a) O-2	$C-H(CH_3)$
	Group	Group	Croup	Croup	Group
o (a,)	1.47348	1,60061	1.82682	1.80717	1.64920
(0,)	1,31468	1.03299	1.35160	1.34431	1.04856
Bond Length $2\omega$ ( $A$ )	1,39140	1.09327	1,43047	1.42276	1,10974
Exp. Bond Length (A)	1.397 avg. (phenol)	1.084 (phenol)			1.11 (avg.) (toluene)
b,c (a,)	0.66540	1.22265	1.22900	1,20776	127295
	0.89223	0.64537	0.73986	0.74388	0.63580
			i		

Table 15.265. The MO to HO intercept geometrical bond parameters of anisole $E_r$ is $E_r$ (nom – atom, msp., AO).	ometrical box	nd parameters of	anisole, E, is	E, ( aom – atom	1, msp. AO).					
Bond	Atom	F. Y	7	E,	Er	Final Total	J. S. S. S. S. S. S. S. S. S. S. S. S. S.	í	E. (124)	E(C2sp
		Bond 1	Bond 2	Bond 3	Bond 4	ते ह	<u>a</u> •	(°	(eV) Final	Find (
"-H (C;H)	ئ.	-0.KS/I35	-0,85035	-0.56690	o	-153.8327	17710.0	0,70597	NEE00.71.	-16,90248
"-H (OC,H3)	C,	-0.72457	6		С	-152,34026	17716.0	0.87495	2503231-	-15,35946
C,=), C,O-C,H,	5	-0,77457	0	•	c	-152.34026	17716.0	0.87495	(15,53033	-15.35%6
C.*), C.O-C.H,	0	4.72457	0.56690	۰	٥		1.00000	OJUMIR	-16.11722	
c,=), c,0c,H,	·	-0.56690	-0.85033	-0.85035	c	-153,88327	17710.0	0.79597	-17,09334	-16,90248
c, =), c, −oc, н,	0	-0.56590	-0.72457	0	0		1.0000	0.84418	-16.11722	
$C_{\kappa} = \int_{\Gamma} C_{\kappa}(\partial C_{\kappa}, H_{\kappa})$	٠,	-0.56690	£035X.0-	-0 15035	0	-(53.8527	17710.0	0.79597	-17.09334	-16,90248

Table 15.264. The energy parameters (eV) of functional groups of anisole.	(eV) of function	al groups of an	solc.		
Parameters	Caup Group	CH (i) Group	C - O (a) Group	C - 0 (b) Group	CH <sub>3</sub> Group
7,	0.75	1			
'u'	2	ı	_	1	3
n3	0	0	0	0	2
n,	0	0	0	0	0
ڻ	0.5	0.75	0.5	0.5	0.75
رة.	0.85252	1	-	1	-
ن ن	-	ı	-	-	1
6,	0.85252	17716.0	0.85395	0.85395	0.91771
טי	0	1	0	0	0
່ ວ່	3	1	ż	2	_
ઈ	0	1	0	0	3
, ''	5.0	51.0	0.5	0.5	0.75
ڻ	0.85252		1	1	-
V, (eV)	-101.12679	-37.10024	-32.67197	-33.15757	-107.32728
V, (aV)	20.69825	13,17125	10.06645	10.12103	38.92728
T (eV)	34.31559	11.58941	8.94231	9.17389	32.53914
V, (eV)	-17.15779	-5.79470	-4.47115	-4.58695	-16.26957
E(mind) (eV)	0	-14.63489	-14.63489	-14.63489	-15.56407
DE Ingino (+11)	0	-1.13379	-1.13379	-1.44915	0
Er (wim) (eV)	0	-13.50110	-13.50110	-13.18574	-15.56407
$E_r(n_2 x x)$ (eV)	-63.27075	-31.63539	-31.63547	-31.63533	-67.69451
$E_{\rm T}(atom - atom, msp^3.AO)$ (eV)	-2.26759	.0.56690	-1.13379	-1.44915	0
$E_{r}(\omega)$ (eV)	-65.53833	-32.20226	-32.76916	-33.08452	-67.69450
a (1013 rad / s)	. 49.7272	26.4826	11.8393	12.0329	24.9286
$E_{K}$ (eV)	32.73133	17.43132	7.79284	7.92028	16.40846
$\widehat{E}_{n}$ ( $\sigma V$ )	-0.35806	-0.26130	-0.18097	-0.18420	-0.25352
$\overline{E}_{K \rightarrow k}$ (eV)	0.19649 [49]	0.35532 Eq. (13.458)	0.13663 [21]	0.13663 [21]	0.3553Z (Eq.
Enc (eV)	-0.25982	-0.08364	-0.11266	-0.11589	-0.22757
Emiz (eV)	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{ m T}({ m circup})$ (eV)	-49.54347	-32.28590	-32.88182	-33.20040	-67.92207
Easter (t. round) (eV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489
Eum (tr. with) (aV)	٥	-13,59844	0	0	-13.59844
$E_{D}(\omega_{\nu \nu})$ (eV)	5,63881	3.90454	3.61204	3.93062	12.49186

mental values [2].	Relative	5
ompared to the experi	Experimental Total Bond Energy	(A)
of Table 15.264 ca	Calculated Total Bond	Energy: (cV)
and the energies	Ger,	7015
and composition	C = () (b) Group	
נוופ זעחכנוטעעו בנינ	C-0 (a)	
calculated using	(J. H.)	j
בי אונים מו שוויפחור	ر <u>∗</u> ر د=ر	١
	Name	ķ
	Formula	C,H <sub>2</sub> O Amis

			j			-	if enter distribution in the late of the												
Alems of Angle	3																		
	: į (°	4 Î G	7 [ 6 g	About	Hydridization Designation	Crambata Atan 3	Atom 2 Hybridization Designation	1 seev	C,	ប	ď	ช	٧.	(eV)	ø, ⊙	9 (5)	(S.)	0 (0	8-
7,707	16900	7					(180E (3.3.A)								_				
(aromatic)	2,44730	4,02,000	4,3383	4.3545 -17,17278	Ä	-17.17211	*	0.79232 0.79232	0,79232	_	_	_	6 707 17	7,050		-	L	<u> </u>	200
70CH										i				DOMOD'I			<u>~</u>	120.19	0
(aromatic)						_									<u> </u>	5.05.	Ŀ		8
											_		-		-	2	=	566	

## **PYRROLE**

Pyrrole having the formula  $C_4H_5N$  comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to a NH functional group. The two symmetrical carbon-to-nitrogen bonds comprise the C-N-C functional group. The 1,3-5 but diene moiety comprises C-C, C=C, and CH functional groups. The C-C and C = C groups are equivalent to the corresponding groups of 1,3-butdiene given in the Cyclic and Conjugated Alkenes section except that the energies terms of the corresponding to oscillation in the transition state match pyrrole. Furthermore, the conjugated double bonds have the same bonding as in 1,3-but diene except that the hybridization terms  $c_2$  of the C-C10 and C = C groups and  $C_2$  and  $C_{20}$  of the C = C group in Eqs. (15.42) and (15.52) become of benzene given that b y Eq. (15.143). $(C_2(benzeneC2sp^3HO) = c_2(benzeneC2sp^3HO) = 0.85252$ ), in the cyclic pyrrole MO which has aromatic character. The bonding in pyrrole, furan, and thiophene are the same except for the energy match to the corresponding heteroatoms. The hybridization permits double-bond 15 character in the carbon-heteroatom bonding.

The NH group is solved equivalently to that of a secondary amine as given in the corresponding section except that the hybridization term  $c_2$  is that of the amino group of aniline in order provide double-bond character to match the group to the other orbitals of the molecule. Similarly, the CH functional group is equivalent to that of 1,3-butdiene, except that  $\Delta E_{H_2MO}(AO/HO) = -2.26758 \, eV$  (Eq. (14.247)) in Eq. (15.42) in order to provide matching double-bond character.

The solution of the C-N-C functional group comprises the hybridization of the 2s and 2p AOs of each C to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs and the nitrogen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the C-N-C-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.52). The hybridization factor  $c_2(arylC2sp^3HO\ to\ N) = 0.84665$  (Eq. (15.152)) matches the double-bond character of the  $C2sp^3$  HOs to the N atom of the NH group, and  $C_2$  and  $C_{2o}$  in Eqs. (15.42) and (15.52).

become that of benzene given by Eq. (15.143),  $C_2$  (benzeneC2sp³HO) = 0.85252. Furthermore,  $\Delta E_{H_2MO}$  (AO/HO) in Eq. (15.42) and  $E_r$  (atom-atom, msp³.AO) in Eq. (15.52) are both -0.92918 eV (Eq. (14.513)) per atom corresponding to -3.71673 eV in total. This is the maximum energy for a single bond and corresponds to methylene character as given in the Continuous-Chain Alkanes section.

The symbols of the functional groups of pyrrole are given in Table 15.267. The structure of pyrrole is shown in Figure 65. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of pyrrole are given in Tables 15.268, 15.269, and 15.270, respectively. The total energy of pyrrole given in Table 15.271 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.270 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrrole determined using Eqs. (15.79-15.108) are given in Table 15.272.

15 Table 15.267. The symbols of functional groups of pyrrole.

Functional Group	· Group Symbol	
$C_a = C_b$ double bond	C = C	
$C_b - C_b$	C-C	
$C_a - N - C_a$	C-N-C	
NH group	NH	$\neg$
СН	СН	

	CH	Group	1.53380	1.01120	1.07021	1.076 (pyrrole)	1.15326	00000
	HIN	Group	1.24428	0.94134	0.996270	0.996 (pyrrole)	0.81370	69736.0
rimental values [1].	C-N-C	Group	1.43222	1.29614	1.37178	1.370 (pyrrole)	0.60931	00000
etrical bond parameters of pyrrole and experimental values [1].	2-2	Group	1.77965	1.33404	1.41188	1.417 (pyrrole)	1.17792	0.74951
geometrical bond paran	C=C	Group	1.45103	1.30463	1.38076	1.382 (pyrrole)	0.63517	0.89910
Table 15.268. The geom	Parameter		a (a <sub>o</sub> )	$c'(a_0)$	Bond Length $2c'(A)$	Exp. Bond Length $(A)$	$b,c$ $(a_0)$	0

יייייייייייייייייייייייייייייייייייייי	200		pyrione. At it and airly! Group and K. K., K. and H. or aikly! groups. E. 13 E. (atom - atom, nity', AO	ı ankyı group an	מע"ע"ע"ע מעפ	A or alkyl gro	ups. 2, 13 C,	atom - atom,	nxy, AO						
Bond	Alon	/;, (e.V.) Bond I	£; (eV) Bond 2	(eV) Bond 3	£, (eV) Bond 4	Final Total Energy ('2xp'	(%)	(°)	E <sub>c. (C2.0°</sub> ) (eV) Final	(eV)	. C	(•)	(•)	d, (o,)	(°)
C-H (C,H)	ن	-1,13340	81626'0-	c	0	-153.67867	17710	0.80561	-16,88873	-16 69786	823	96.64	73.67	5701	
C-H(C,H)	ئ	-1,13380	-1.13380	0	٥	-153,88328	17716.0	0.79597	-17,09334	-16.90248	12.21	2, 78	1 2	20011	16670.0
$C_{\mu} = (H)C_{\mu} - C_{\mu}(H) = C_{\mu}$	c,	-1,133X0	-1,13380	0	٥	-153.88328	17110	0.79597	-17.09334	-16.90248	7516	11.43	42.40	13124	F. 15.7
$C_s = C_s(H)(H)C_s = C_s$	ູ້	-1,13310	OKEET'1		٥	-153.88328	17716.0	0.79597	-(7.09334	-16,90248	136.36	43.64	9105	0.77857	2000
$HNC_{*} = C_{*}(H)$	ڻ.	-1,13380	K16ZEO-	٥		-153,67867	177160	0.80561	-16,88873	-16.69786	136.75	63.3	31.5	PALIE O	200000
$C_{\bullet}(H)N-C_{\bullet}=C_{\bullet}(H)$	C,	-4.13380	-0.92918	٥.		-153.67267	17714.0	0.80561	-16.88873	-16,69786	138.54	4 46	61.09	S COY O	ALIONO.
$C_{\bullet}(H)N - C_{\bullet} = C_{\bullet}(H)$	×	-0,92918	-0.92918	0	c		0.93084	0.81549	-16,68411		138.92	41.08	61.59	0.68147	0.61467
N-H (NH)	N	#1626'0"	. #1626'0	Q	c		0.93084	0.81349	-16,68431	-	117.34	62.66	62.90	0.56678	0.37456

Table 15.270. The energy parameters (eV) of functional groups of pyrrole.

Parameters	C = C	C-C	C-N-C	NH	СН
	Group	Group	Group	Group	Group
<i>n</i> <sub>1</sub>	2	]	2	1	<u> </u>
n <sub>2</sub>	0	0	0	0	0
<i>n</i> <sub>3</sub>	0	0	0	0	0
<i>C</i> ,	0.5	0.5	0.5	0.75	0.75
C <sub>2</sub>	0.85252	1	0.85252	0.93613	1
<i>c</i> <sub>1</sub>	1	1	1	0.75	1
<i>c</i> <sub>2</sub>	0.85252	0.85252	0.84665	0.92171	0.91771
<i>c</i> <sub>3</sub>	0	0	0	1	1
C <sub>4</sub>	4	2	4	1	I
<i>c</i> <sub>5</sub>	0	0	0	1	1
$C_{i_{\bullet}}$	0.5	0.5	0.5	0.75	0.75
C <sub>20</sub>	0.85252	1	0.85252	1	1
V <sub>c</sub> (eV)	-104.37986	-33.80733	-106.58684	-39.48897	-39.09538
V, (eV)	20.85777	10.19898	20.99432	14.45367	13.45505
T (eV)	35.96751	9.49831	37.21047	15.86820	12.74462
$V_{m}(eV)$	-17.98376	-4.74915	-18.60523	-7.93410	-6.37231
E(лотно) (eV)	0	-14.63489	0	-14.53414	-14.63489
$\Delta E_{H_2MO}(AOIHO)$ (eV)	-2.26759	-1.85836	-3.71673	0	-2.26758
$E_{T}(AOTHO)$ (eV)	2.26759	-12.77653	3.71673	-14.53414	-12.36731
$E_T(H_2MO)$ (eV)	-63.27075	-31.63572	-63.27056	-31.63534	-31.63533
$E_T(atom-atom, msp^3.AO)$ (eV)	-2.26759	-2.26759	-3.71673	0	0
$E_{\tau}(\mu o)$ (eV)	-65.53833	-33.90295	-66.98746	-31.63537	-31.63537
$\omega \left(10^{15} \ rad \ / \ s\right)$	15.4421	12.3131	15.7474	48.7771	28.9084
$\mathcal{E}_{K}(eV)$	10.16428	8.10471	10.36521	32.10594	19.02803
$\overline{\widetilde{E}}_{D}$ (eV)	-0.20668	-0.19095	-0.21333	-0.35462	-0.27301
$\bar{E}_{_{Rvib}}$ (eV)	0.17897 [6]	0.14829 [48]	0.11159 [12]	0.40696 [24]	0.39427 [56]
$\bar{\mathcal{E}}_{osc}(eV)$	-0.11720	-0.11680	-0.15754	-0.15115	-0.07587
Emag (eV)	0.14803	0.14803	0.14803	0.14803	0.14803
$E_{\gamma}(Grap)$ (eV)	-65.77272	-34.01976	-67.30254	-31.78651	-31.71124
Einnial (c. AOTHO) (eV)	-14.63489	-14.63489	-14.63489	-14.53414	-14.63489
$E_{initial}(c, AOIHO) (eV)$	0	0	0	-13.59844	-13.59844
$E_{D}(Gmp)$ (eV)	7.23317	4.74998	8.76298	3.51208	3.32988

values (2).	}		
experimental	Relative		-0,00057
5.270 compared to the	Experimental Total Bond Energy	(eV)	44.785
gies of Table 1.	Calculated Total Boad	Encret: (cV)	44,81090
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Table 15.271.		N.H.C	

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ZHC, N	1.02241	1.59228	4 0166	-14 82575	-	-14.53414	z	17716.0	171260	67.0	-	57.0	1,00435	0		-	1 2	120.51	121.5
ZC,C,H,			L						7						<u> </u>	+	-		(Systems)
ZHW."	I.MZKR	2.5922X	3,8987	-14.53414	z	-16,49325	vs.	0.84665 (Eq.	0.82493 (Eq.	6.73	-	27.0	0.97433	0		15021	25.701	75.037	
73'.5'HZ	1,02241	2 66307	4,2111	-16,XKH73	22	-15.95954 C.	75	0.80561	0.85232	6.73	-	0.73	1.05822	۰		$\dagger$	-	127.20	127.1
ZH,C,C,	2.02241	2.60925	4.2111	-16,xxx73	2	15.95934 C	y	0.80561	0.85252	67.0	-	0.73	1.05822			+	+	25.05.1	(pixtolc)
".J":ZH7	2.02241	2,60925	4.1312	-17,09334 C.	×	-1647951	=	10207.0	0.12562	67.0	-	6.75	527.00.1			+		135.76	
'', '', '', '', '', '', '', '', '', '',												T	1			37.76	1020		127.1
ZNC,C,	2.5922K	2,60925	4.1932	-14.53414	2.	-17.09334 C,	=	0.84665 (Eq	0.79597	-	-	-	0.82131	-1.44915				10752	(pvmde) 107.7
ZY."NC.	2.5922K	2.5922K	4,2426	-17,41791	326	12,81791	97	0.76360	0.76360	-	-	-	0,76360	-1,75236	}	+	1 8	100	109.8
, 'C,'C,'	2.60725	2.66807	42426	-17.KI791	3.6	-1K.02252	29	0.76360	0,75493	-	-	-	0,75927	-1.85136	-	+		$\downarrow$	(pymale) 107.4
															_	_	-		(chample)

## **FURAN**

Furan having the formula  $C_4H_4O$  comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to an oxygen atom. The two symmetrical carbon-to-oxygen bonds comprise the C-O-C functional group. The 1,3-butdiene moiety comprises C-C, C=C, and CH functional groups. The CH, C-C, and C=C groups are equivalent to the corresponding groups of pyrrole given in the corresponding section.

The C-O-C functional group of furan is solved in a similar manner as that of the C-N-C group of pyrrole. The solution of the C-O-C functional group comprises the hybridization of the 2s and 2p AOs of each C to form a single  $2sp^3$  shell as an energy 10 minimum, and the sharing of electrons between two  $C2sp^3$  HOs and the oxygen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the C-O-C-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.52). The hybridization factor  $c_2(arylC2sp^3HO\ to\ O) = 0.79329$  (Eq. (15.150)) matches the double-15 bond character of the  $C2sp^3$  HOs to the O atom, and  $C_2$  and  $C_{2o}$  in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143),  $C_2(benzeneC2sp^3HO) = 0.85252$ . Furthermore,  $E_T(atom-atom, msp^3.AO)$  in Eq. (15.52) is  $-0.92918\ eV$  (Eq. (14.513)) per atom corresponding to  $-3.71673\ eV$  in total.

The symbols of the functional groups of furan are given in Table 15.273. The 20 structure of furan is shown in Figure 66. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of furan are given in Tables 15.274, 15.275, and 15.276, respectively. The total energy of furan given in Table 15.277 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.276 corresponding to functional-group composition of the molecule.

25 The bond angle parameters of furan determined using Eqs. (15.79-15.108) are given in Table 15.278.

upe of furan.	Group Symbol	2=2	ر.–ر	J-0-D	H.J
Table 15.273. The symbols of functional groups of furan.	Functional Group	$C_n = C_n$ double bond	C. – C.	<b>ジーローご</b>	-

reters of furan and experimental values [1],  Cricup Cricup 1.7796.5 1.41846 1.33404 1.38854 1.41188 1.36373 1.4719 1.4719 1.17792 0.58853	In d parameters of firms and experimental forces (1.7796.5 (1.7796.5 (1.7796.5 (1.7796.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790.5 (1.7790
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			10	5	4	1830 Fund			E. (C2.07)	5	è	٩	0	,	[
		S S	(8)	Ş	3	Energy	!	!	15	1 492)	. :	5 ;	5"	<b>5</b>	φ.
		Bond I	Bond 2	Bond 3	Bond 4	Czzy	(*)	(°	Fine	કું <sub>,</sub>	0	Ξ	$\overline{\mathbb{C}}$	(°)	(0,)
						§			!	Fina					•
C-H (CH)	٠,	-1.13380	-0.92918	0	0	-153,67857	0.91771	0 80561	-16.88875	16 40704	,,	1			
C-H (CH)	į	00111							200001	001/07/01	62.33	20.03	43.94	1.10452	0.09331
(t v)	•	-1.15580	-1.13380		0	-153.88328	0.91771	0.79597	-17,09334	-16.50248	82.21	97.79	71 29	1 11014	702010
$\mathcal{L} = (H) \mathcal{L} = \mathcal{L}(H) = \mathcal{L}$		04.41	00000											- 1314	\$ 25.5
" ( . ) ( . ) " " " " " " " " " " " " " " " " " "	•	-1.13380	1.13380		•	-153.88328	17716.0	0.79597	-17,09334	-16.90248	55 16	88.42	07.07	366161	
(. m(. (H)(H)(. m(.		1 13100										2.00	74.77	1.31420	0.021//
"	•	1.13380	-1.15380	0	•	-153.88328	17716.0	0.79597	-17.09334	-16.90248	136.36	43.64	98 65	0.72867	202530
$(\mathcal{K}_{\perp} = C_{\perp}(H))$	_	111380	0.0000		ĺ								20:22	1.72037	0.57000
			0.72710	,	- i	133.0/80/	0.91771	0.80561	-16.88873	-16.69786	136.75	43.25	8038	0.71784	2C785 0
CO - C' = C'(H)	ر. ان	-1.13380	-0.92918	0	0	-153,67867	17710	0 80561	-16 88873	30702.	21.071	2000			2000
(.0-0. =0. (#)	[									00/60:01-	140.10	29,84	27.50	0.66992	0.61862
, ,	c	-0.92918	-0.92918	0	0		000001	0,81549	-16.68417		140 57	20.49	25.5	20000	1
											4.10.00	22,70	7770	0.63300	U.02947

Table 15.276. The energy parameters (eV) of functional groups of furan.

Parameters	C = C Group	C-C Group	C-O-C Group	<i>CH</i> Group
$n_1$	2	1	2	}
$\overline{n_2}$	0	0	0	. 0
n,	0	0	0	0
<i>C</i> ,	0.5	0.5	0.5	0.75
$C_2$	0.85252	1	0.85252	1
c <sub>1</sub>	1	1	1 .	1
$c_2$	0.85252	0.85252	0.79329	0.91771
$c_3$	0	0	0	1
c <sub>4</sub>	4	2	4	1
c <sub>s</sub>	0	0	0	. 1
$C_{1o}$	0.5	0.5	0.5	0.75
$C_{2\sigma}$	0.85252	1	0.85252	1
V <sub>e</sub> (eV)	-104.37986	-33.80733	-102.49036	-39.09538
$V_{p}(eV)$	20.85777	10.19898	21.11822	13.45505
T(eV)	35.96751	9.49831	36.20391	12.74462
$V_{n}(eV)$	-17.98376	-4.74915	-18.10196	-6.37231
E(AOIHO) (eV)	0	-14.63489	0	-14.63489
$\Delta E_{H_2MO}(AOIHO)$ (eV)	-2.26759	-1.85836	0	-2.26758
$E_{\tau}(AOIHO)$ (eV)	2.26759	-12.77653	0	-12.36731
$E_{\tau}(H_1MO)$ (eV)	-63.27075	-31.63572	-63.27019	-31.63533
$E_T(atom-atom, msp^3.AO)$ (eV)	-2.26759	-2.26759	-3.71673	0
$E_r(MO)$ (eV)	-65.53833	-33.90295	-66.98746	-31.63537
$\omega \left(10^{15} \ rad \ / \ s\right)$	15.4421	12.3131	58.0664	28.9084
$E_{\kappa}^{\cdot}(eV)$	10.16428	8.10471	38.22034	19.02803
$\bar{E}_{D}(eV)$	-0.20668	-0.19095	-0.40965	-0.27301
$\overline{\overline{E}}_{Krih}(eV)$	0.17897 [6]	0.14829 [48]	0.12523 [57]	0.39427 [56]
$\vec{E}_{usc}$ (eV)	-0.11720	-0.11680	-0.34704	-0.07587
$E_{mag}(eV)$	0.14803	0.14803	0.14803	0.14803
$E_{r}(irmp) (eV)$	-65.77272	-34.01976	-67.68154	-31.71124
Einling (c. AOTHO) (eV)	-14.63489	-14.63489	-14.63489	-14.63489
$E_{ininal}(c, AOIHO) (eV)$	0	0	0	-13.59844
$E_{D}(cornp) (eV)$	7.23317	4.74998	9.14198	3.32988

functional group composition and the energies of Table 15.276 compared to the experimental values [2].	
ted using the	
energies of furan calcula	
77. The total bond	
Table 15.27 Formula	

			1	-		4	41.67782	782	41.692		0.00033	1	j	;					
Table 15.278. The bond angle parameters of furan and experimen	ingle param	iders of fi	uran and	experimenta	ital values [1]. In the calculation of $\theta$ , the narrameters from the measuring	calculation	of $\theta$ , the namen	ere from th			-	, ,		15					
Anthu of Angle	25.	2c'	20.	E	Atom !	11	Atom 2		breeding.	angic were	used. Er	15 L <sub>T</sub> (al.	m ~ alom, n		ď.				
	(a, )	(a)	Terminal Atomy (a <sub>0</sub> )	Alom 1	Hybridization Designation	- Corbride Atom 2	Hybridization Designation	Am 5.	C <sub>2</sub>	ᠸ	౮	ۍ	יטי	£7. (eV)	ø, ©	6 O	0° ©	(a)	Εκρ. (°)
ZHC.O	2,02281	2 \$ 7707	100	1,699	148015 (3.3.5)		(Table (5.3.B)		0.79329								:		
			$\overline{}$	-	2	-13.61806	0	0.8056?	ន	0.73	-	0.75	0.98470	•	_				115.9
ZC,C,H,									(051.51)							7		30.71	(fuery)
JJH				-16.88873		1505051.										117.02	110.69	132.29	
1.3 41.12	77207	2,66807	4.2269	ť	13	ڻ ٽ	v	0.80561	0.83252	6.73	-	0.75	1.05822	c		$\dagger$	+		1280
, ZH, C, C,	20241	2 60925	4 7760	-16.88873		-15.95954				1				,		_	_	128.09	(furan)
			_	٠.	2	ຜ່	•	0.80561	0.85252	0.75	-	0.75	1.05822				-		
"2'L'C"	2.02241	2.60925	4,1312	-17.09334	8	-16.47951	:					1			1	7		25 15	
				-		ن	=	0,79597	0.82562	27.0	-	075	1.03725	•			_	125.76	
ζ, ', ', ', ', ', ', ', ', ', ', ', ', ',										1	Ī		1		1	1	1		
7C.C.0	3,6000			-17.09334			. a		0 70130						-	125.76	107.01	127.23	128.0
	4,007	4,000,00	4.2567	ڻ	8	-13.61806	0	0.79597	E .	_	-	_	D 76467	1 46376		-	-	-	
.w	257707	2,57707	4.1201	-18,22713	og Og	-18 22717	5		(13.150))	1	1			orces.	7		-	10.69	(furm)
10'0'07	2,60925	2 60807 42476 17 51 TO	47076	100 10 41	,		*	0.74080	0.74090	-	-	-	0.74646	-1.85836			=	106.25	106.6
			,	16/19/	97	-18 02252 I	•	20000		-	-							-	(6223)

#### THIOPHENE

Thiophene having the formula  $C_4H_4S$  comprises the conjugated alkene 1,3-butdiene that forms a cyclic structure by terminal-atom bonding to an oxygen atom. The two symmetrical carbon-to-oxygen bonds comprise the C-S-C functional group. The 1,3-butdiene moiety comprises C-C, C=C, and CH functional groups. The CH, C-C, and C=C groups are equivalent to the corresponding groups of pyrrole and furan given in the corresponding sections.

The C-S-C functional group of thiophene is solved in a similar manner as that of the C-N-C group of pyrrole and the C-O-C group of furan. The solution of the C-S-C functional group comprises the hybridization of the 2s and 2p AOs of each C to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between two  $C2sp^3$  HOs and the oxygen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. Thus, the C-S-C-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.52).

In thiophene, the energy of sulfur is less than the Coulombic energy between the electron 15 and proton of H given by Eq. (1.243). Thus,  $c_2$  in Eq. (15.52) is  $c_2(benzeneC2sp^3HO) = 0.85252$  to match the double-bond character of the  $C2sp^3$  HOs, and the energy matching condition is further determined by the  $C_2$  parameter. Using the energy of S,  $E(S) = -10.36001 \, eV$  in Eq. (15.68) and the  $C2sp^3$  HO energy of  $E(C,2sp^3) = -15.76868 \, eV$  (Eq. (15.18) corresponding to s=2 in Eqs. (15.18-15.20), the 20 hybridization factor  $C_2$  of Eq. (15.52) for the C-S-C-bond MO is

$$C_2(S3p \text{ to aryl-type } C2sp^3HO) = \frac{E(S,3p)}{E(C,2sp^3)} = \frac{-10.36001 \text{ eV}}{-15.76868 \text{ eV}} = 0.65700$$
 (15.153)

 $C_{1o}$  is also given by Eq. (15.153). Furthermore,  $\Delta E_{H_2MO}(AO/HO)$  of the C-S-C-bond MO in Eq. (15.42) and  $E_r(atom-atom,msp^3.AO)$  in Eq. (15.52) are both -0.72457~eV per atom corresponding to -2.89830~eV in total. The energy contribution equivalent to that of 25 a methyl group (Eq. (14.151)) and that of the C-S-bond MO of thiols given in the corresponding section matches the energy of the sulfur atom to the  $C2sp^3$  HOs.

The symbols of the functional groups of thiophene are given in Table 15.279. The structure of thiophene is shown in Figure 67. The geometrical (Eqs. (15.1-15.5) and (15.42)),

intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of thiophene are given in Tables 15.280, 15.281, and 15.282, respectively. The total energy of thiophene given in Table 15.283 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.282 corresponding to functional-group composition of the molecule. The bond angle parameters of thiophene determined using Eqs. (15.79-15.108) are given in Table 15.284.

Table 15.279. The symbols of functional groups of thiophene.

Functional Group	Group Symbol
$C_a = C_b$ double bond	C = C
$C_b - C_b$	C-C
$C_a - S - C_a$	C-S-C
СН	СН

1.08953 1.11914 1.31226 0.72857

(a, d,

(a) (d)

	_							
	CF.	Group	1.53380	1.01120	1.07021	1.078 (thiophene)	1.15326	0,66030
rperimental values [1]	C-S-C	Group	1.74058	1.62766	1.72264	1.714 (thiophene)	0.61671	0.93513
racie 19.280. The geometrical bond parameters of thiophene and experimental values [1]	υ <u>-</u> υ	Group	1.77965	1,33404	1.41188	1.423 (thiophene)	1.17792	0.74961
Scometrical bond param	)=C	Group	1.45103	1.30463	1.38076	1.370 (thiophene)	0.63517	0.89910
1401E 13.280. INC	Parameter		a {u,}	$c'(o_a)$	Bond Length 2c' (A)	Exp. Bond Length (A)	h,c (u <sub>0</sub> )	υ

Bard	comemeat	oond parameter.	convention bond parameters of thiophene. $R_i$ is an alkyl group and $R_iR_iR^n$ are $H$ or alkyl groups. $E_i$ is $E_i$ (aron-aron, $m_iR_iR_iR_i$ ).	R, is an alkyl g	roup and R,R',	,R" are H or a	lkyl groups.	$E_r$ is $E_r(ato)$	111 – olom, msp. <sup>3</sup>	.40).			
	Atom	E.	Er	E, .	$E_{r}$	Final Total	7	'Ann	[c.m(C24)]	$E(C2x\sigma^3)$	.0	9	9
		Bond 1	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	C2xp <sup>3</sup>	(°)	(°)	(eV) Final	(eV)	•	- C	~ ©
(H J) H - J	1					ĘŞ							
	,	-1,13380	-0.72457	0	•	-153.47406	0,91771	0,81549	-16.68412	-16.49326	84.49	15 50	14.7
C-H(C,H)	ن- -	-1.13380	-1.13380	0	٥	-151.88328	17.100	7030F A	7,000 5.				
C = (H)C - C(H) = C	į	98.5.							+CC/0'/1-	-10.90248	12.21	97.79	49.7
		1,13380	-1.13380	0	c	-153.8832B	0.91771	0 79597	-17.09334	.16.90248	75.19	88.43	12.60
$( \mathcal{L}_{\mathcal{L}}(H)/H) ( \mathcal{L}_{\mathcal{L}}(H)) $	ڻ	-1.13380	-1.13380	•	0	-153,88328	0.91771	0.795.07	17.00114	27,000,71			
$SC_s = C_s(H)$		narri I.	0.77467	ļ					257.00	10.0044	136.30	43.64	59.86
(11) 11 11 11			100	۶	٥	-153.47406	0.91771	0.81549	-16 68412	-16,49326	137.14	42.86	50.83
(")" - " - (")	ر.	-1.13380	-0.72457	•	0	-153,47406	0,91771	0.81.549	-16.68417	25,000,31			
(L'.S-C. = C.(H)	3	0 77457		,						Dacer.01-	75.141	38.48	8236
	:		15.77.0.		•		13201	OBJEO	407467				

table 13,262. The energy parameters (ev.) of tunctional groups of thioppienes.	וז (כיין טו ומווכמטנ	al Eleups of things	icuo.	
Parameters	ე≖ე Gronb	C'-C Group	C-S-C Group	Group
$u^{l}$	2	1	2	-
$n_1$	0	0	0	0
n,	0	0	0	0
Ն	0.5	0.5	0.5	0.75
5	0.85252	-	0.65700	-
'5	-	1	1	. 1
· ·	0.85252	0.85252	0.85252	0.9177
S	0	0	0	-
'2	4	2	4	-
63	0	0	0	1
ر.''	0.5	0.5	5.0	0.75
C3,	0.85252	1	00/59'0	-
V, (aV)	-104.37986	-33.80733	-96.78916	-39.0953
V, (eV)	20.85777	10.19898	16.71820	13.4550
T (aV)	35,96751	9.49831	27.80371	12.7446
V. (aV)	-17.98376	4.74915	-13.90186	-6,3723
fil.o.no) (eV)	0	-14,63489	0	-14,6348
ΔΕ <sub>11,10</sub> (10 in) (eV)	-2.26759	-1.85836	-2.89830	-2.2675
12 (no m) (AN)	2.26759	-12.77653	2.89830	-12.3673
$E_{\mathbf{r}}(u,\omega)$ (eV)	-63.27075	-31,63572	-63,27080	-31.6353
$E_T(\omega \iota \circ m - \alpha \iota \circ m, m \times \rho^2, A\Omega)$ ( $\omega V$ )	-2.26759	-2,26759	-2.89830	0
Ry (10) (aV)	-65.53833	-33.90295	-66.16903	-31,635
ω (1013 rad/x)	15.4421	12,3131	10,3184	28.908
$E_{\kappa}\left(eV ight)$	10.16428	8.10471	6.79173	19.0280
$\vec{E}_n$ ( $eV$ )	-0.20668	-0.19095	-0.17058	-0.2730
E (eV)	0.17897	0.14829	0.08146	0.39427
E. (0V)	-0.11720	-0.11680	-0.12985	-0.0758
$L_{\rm topp}$ $(eV)$	0.14803	0.14803	0.14803	0.1480
Fy (timy) (eV)	-65.77272	-34,01976	-66.42873	-31.7112
12 (cr. 10 110) (cV)	-14.63489	-14.63489	-14.63489	-14,6348
Esser (c. 10 no) (aV)	0	0	0	-13,5984
Epliams (CV)	7.23317	4,74998	71688.7	3,3298

he experimental values [2].	
82 compared to t	Relative
ics of Table 15.2	Experimental
omposition and the energ	Calculated
Troup co	3
ng the functional	シークーン
calculated us	ָ כו
ies of thiophene	)
Name	
Formula	

				a				P			(g.					- 19	-	(B)		(thio
				Cal. 0	€		1	8281	124 58	07.57	124.58	1	127.57	22.13		123.27		<u> </u>	2 2	
				6					13.22							113.60			l	
				6	<u></u>				119.58						1	13.13			Ī	
				0,	©															
			com, msp. AC).	ਸ਼ <b>,</b>	(e)		c	,			,	c	,	0			-50 77467	4.15431	-1.85836	
		,	r ( arom – a	75			0.87495			1 04540		1.04540		1.02453	Ī		0.71030		0.81549	
		.!	54 IS E	5			0.75			1,0		6.75		0.75			-		_	T
		Post and the	vice ascu.	Ն			(F)	15.126))		-		_		-			L.65700	(15.133))	_	
Emor	0 00013	adine onela	rama ama	ᠸ			27.0			0.75		0.75		0.75			-		-	
Æ		n the pre-		C <sub>2</sub>		13.00	2 2 2	15.126))	į	0.85252		0.85252		0.81549		000000	Eq.	(15.153))	0.81549	
Total Bond Energy (eV)	40.430	ameters from		چ Aem i		2002.0	ផ្ទ	(15.65))		0.81549		0.81549		0.79597			0.76360		0.81549	132.0
<b>9</b> (	40.42501	tion of $\theta$ , the par		Hybridization	Table 14 3 By	(12016 1913.D)	Ø			٧		9		<u>*</u>			s		14	o,
	4	in the calcula		Contracts Aum 2			-10,36001			-15.95954	13.95954	ປ	-16.68412	ئ.			1036.01-		.16.68412	-18 02752
		ental values [1]. 1	Aborn	Hybridization	(Table 15.3 B)		•			4		7					7.2		•	2
		ınd experim		Contends Alon I			-15.55033		2000	-10.08412	-16.68412	υ,	-17.09334	ů,		17.81791	ບ	21.02.21	71.00.01-	-16.88873
		iophene a	-5.5	Tomical	(0)		4.6030			4.1633		4. 183	4 0825				4.9809	4 7069		4.4159
-	1	ters of th	,	Bend 2	1561		3.25533		T	2.66807		2.60925	2,60025			Ī	3.25533	175511		2,66807
		igle parame	20,	Berdi	(0,		2,02241			102241	1,600	167707	2.02241	7			2.60925	1,759.1		2.60725
C.H.S Thirefore		Table 15.284. The bond angle parameters of thiophene and experimental values [1]. In the calculation of 8., the parameters from the neconcline many and the first from the neconcline many and the first from the neconcline many and the first from the neconcline many and the first from the neconcline many and the first from the neconcline many and the first from the neconcline many and the first from the neconcline many and the first from the neconcline many and the first from the neconcline many and the first from the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline many and the neconcline m	Atmes of Angle				מ"ר"	4C,C,H_		ZH,C,C,	JJHI	1,000	7H,C.,C.		ZC,C,H,	0.0.0	در" ۲۰۰۰	3C 3C		ZC,C,C

# **IMIDAZOLE**

Imidazole having the formula  $C_3H_4N_2$  comprises a conjugated system that is equivalent to pyrrole with one of the conjugated CH groups replaced by a nitrogen atom. The CH, NH, and C = C groups are equivalent to the corresponding groups of pyrrole, 5 furan, and thiophene where present. In addition, the nitrogen substitution creates a C-N=C moiety comprising C-N and N=C functional groups. The C-N bonding is the same as that of a tertiary amine except that the hybridization term  $c_2$  in Eqs. (15.42) and (15.52) is that of the amino group of aniline,  $c_2(arylC2sp^3HO\ to\ N) = 0.84665$  (Eq. (15.152)). The hybridization factor provides double-bond character to match the group to the  $\Delta E_{H,MO}(AO/HO)$  in Eq. (15.42) and 10 other orbitals of the molecule.  $E_T(atom-atom, msp^3.AO)$  in Eq. (15.52) are both -0.92918 eV (Eq. (14.513)). This matches the energy of the group to that of the contiguous N=C group wherein  $\Delta E_{H,MO}(AO/HO)$  in Eq. (15.42) and  $E_{\tau}(atom-atom,msp^3.AO)$  in Eq. (15.52) are both -0.92918 eV (Eq. (14.513)) per atom of the double bond with aromatic character as in the 15 case of the prior heterocyclic compounds. As in the prior cases of pyrrole, furan, and thiophene,  $n_1 = 2$  and  $C_2$  and  $C_{2o}$  are the same as  $C_2$  (benzeneC2sp<sup>3</sup>HO) = 0.85252 (Eq. (15.143)) in Eqs. (15.42) and (15.52). To match the energy of the nitrogen to the C2sp3 HO,  $c_2$  of the N=C-bond MO is also given by Eq. (15.152). These parameters also provide an energy match to the C-N-C group.

As in the case of pyrrole, the C-N-C-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.52). The hybridization factor  $c_2(arylC2sp^3HO\ to\ N) = 0.84665$  (Eq. (15.152)) matches the double-bond character of the  $C2sp^3$  HOs to the N atom of the NH group, and  $C_2$  and  $C_{20}$  in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143),  $C_2(benzeneC2sp^3HO) = 0.85252$ . Furthermore,  $\Delta E_{H_1MA}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom, msp^3.AO)$  in Eq. (15.52) are both  $-0.92918\ eV$  (Eq. (14.513)) per atom corresponding to  $-3.71673\ eV$  in total.

The symbols of the functional groups of imidazole are given in Table 15.285. The structure of imidazole is shown in Figure 68. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of imidazole are given in Tables 15.286, 15.287, and 15.288, respectively. The total energy of imidazole given in Table 15.289 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.288 corresponding to functional-group composition of the molecule. The bond angle parameters of imidazole determined using Eqs. (15.79-15.108) are given in Table 15.290.

10 Table 15.285. The symbols of functional groups of imidazole.

Functional Group	Group Symbol
$C_a = C_b$ double bond	C = C
$N_b = C_c$ double bond	N = C
$C_b - N_b$	C-N
$C_o - N_o - C_c$	C-N-C
$N_{\mathfrak{o}}H$ group	NH
СН	СН

	H)	Group	1,53380	1.01120	1.07021	1,076 (pymole)	1.15326	0.65928
	HN	Group	1.24428	0.94134	0.996270	0,996 (pymole)	0.81370	0.75653
	こ - メーン	Group	1.43222	1,29614	1,37178	1.370 (pyrrole)	0.60931	0.90499
COUNTY NAMES IN	メーン	Group	1.82450	1.35074	1,42956	·	1.22650	0,74033
CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR OF THE CONTRACTOR O	V=√	Group	1.44926	1,30383	137991		0.63276	0.89965
able 12.200. The Fault delical boild parameters of influezone and experimental values	<b>2</b> =2	Group	1.45103	1,30463	1.38076	1.382 (pynole)	0.63517	0.89910
1401C 13.500, 11K	Parameter		(°o) o	(°, (°)	Bond Length 2c' (A)	Exp. Bond Length (A)	h,c (a,)	ъ

0.89910	0.89965	65	0.74033	0.90	0.90499	0.75653		0.65928	7						
Table 15.287. The MO to HO intercept geometrical band parameters of imidazole. R, is an alkyl group and R,R',R" are H or alkyl groups. E, is E, (aron - drom, msp', AO)	netrical bonc	1 parameters of i	midazole. R, is	an alkyl group a	and R.R.R" ar	e H or alkyl ga	roups. Er is &	E, (atom – oton	, msp . 40).						
Bond	Atom	F. (6V)	1. L.	E <sub>T</sub> .	Er (eV)	Final Total Energy	][	3	E(C2rp')	E(C2sp2)	.6	9.3	, e	<i>d</i> .	, d
		Bond I	Bond 2	Bond 3	Bond 4	(2xp)	(a)	(%)	Final	(cv) Final		5		(°a)	(%)
$C-H\left(C,H\right)$	.,	-1.13380	-0.92918	0	0	-153.67867	17716.0	0.80561	-16.85873	-16.69786	83.35	96.63	43.94	1.10452	0.09331
C + H(C, H)	ť	-1.13380	-0.46459	O	o	153.21401	17716.0	0.82840	-16.42414	-16.23327	85.93	94,07	45.77	1.06995	0.05875
C-H (C,H)	ن:	-0.92918	-0.92918	0	0	\$0745.621-	17116.0	0.81549	-16.68411	-16.49325	84,49	15.26	44.47	1.08933	0.07833
$C_s = (H)C_s - \overline{N}_s = C_s$	ر: ا	-0.46459	-1.13380	0 .	0	10717151-	17719.0	0.82840	-16.42414	-16.23327	90.36	19.64	42.49	1,34547	0.00527
$C_s = \{H\}C_s - N_k = C_s$	ž	-0.46459	-0.92918	c	0		0.93084	0.83885	-16.21953		51,19	\$8.68	43.14	1,33135	0.01939
$C_{\mu} = C_{\mu}(H)N_{\mu} = C_{\mu}$	ن	-1.13380	-0,46459	0	0	-153.21408	0,9177[	0.82840	-16.42414	-16.23327	137,64	42.16	61.49	0.69250	0.61213
$HN_{C_s} = C_s(H)$	: "	-1.13380	-0.92918	0	0	-153.67867	0.91771	0,80361	-16.88873	-15.69786	136.73	43.25	60,35	0.71784	0.58678
$C_{r}(H)N_{s}-C_{s}=C_{s}(H)$	ن:	-1.13380	81626.0-	٥	0	-153,67867	0,91771	0.80561	-16.88873	-16.69786	138.54	41.46	60'19	0.69238	0.60376
$C'(H)N_x - C_x = C_x(H)$	≥,	-0.92918	-0.92918	۰	٥		0.93084	0.81549	-16.68411		138,92	41.03	61.39	0.63147	0.61457
N-H (N,H)	۲,	-0.72918	-0.92918	۰	0		0 93084	0.81549	-16.68411		117.34	9979	62.90	0.5667B	0.37456
$(H)C_c - N_aC_a = C_a(H)$	ئن	-0.92918	-0.92918	•	٥	.153,47405	0.91771	0.81549	-16.68411	-16.49325	138.92	41.08	61.59	0.68147	0.61467
$C_{\mu} = (H)C_{\mu}N_{\mu} = C_{\mu}$	ن	-0.02918	-0.92918	•	٥	-153.47405	0,91771	0.81549	-16.68411	-16.49325	137,31	42.69	60,92	0,70446	0.59938
$C_{s} = (H)C_{s}N_{s} = C_{s}$	₹	-0.03918	-0.46459	۰			0.93084	.0.83885	-16 21953		138.20	41.80	62.08	0.67849	0.62534

Table 15,288. The energy parameters (eV) of functional groups of imidazole.	ers (eV) of function	al groups of imid				
Parameters	C=C Group	N ⊌ C Group	Z- × Cuonb	Group	N.H. Group	CH.
'n	2	7	-	2	-	-
n,	0	0	٥	0	0	0
n,	0	0	0	0	0	0
C <sup>1</sup>	0.5	0.5	0.5	0.5	0.75	0.75
<u>ن</u>	0.85252	0.85252	_	0.85252	0.93613	-
5	1	1		~	0.75	-
c <sub>1</sub>	0.85252	0.84665	0.84665	0.84665	171260	0.91771
ซ์	0	0	0	0	1	-
<i>c</i> ,	4	7	7	4	-	-
5	0	0	0	0	-	_
¢,,	0.5	0.5	2.0	50	0.75	0.75
5.	0.85252	0.85252	-	0.85252	-	_
V, (aV)	-104.37986	-103.92756	-32.44864	-106,58684	-39.48897	-39.09538
V (cV)	20.85777	20,87050	10,07285	20.99432	14.45367	13.45505
T (eV)	35.96751	35,85539	8,89248	37.21047	15.86820	12.74462
V, (cV)	-17.98376	-17,92770	4.44624	-18,60523	-7,93410	-6.37231
E(10:10) (UV)	0	0	-14,63489	0	-14.53414	-14.63489
ΔΕ, 20 (w w) (eV)	-2.26759	-1.85836	-0.92918	-3.71673	0	-2.26758
E. [mu] (eV)	2.26759	1.85836	-13.70571	3.71673	-14,53414	-12.36731
E_ (u, m) (cV)	-63.27075	-63.27100	-31.63527	-63,27056	-31,63534	-31.63533
$E_T(alom - alom, msp^1.AO)$ (eV)	-2.26759	-1,85836	81676'0-	-3,71673	0	
12, (sr) (cV)	-65.53833	-65,12910	-32.56455	-66.98746	-31.63537	-31,63537
Φ (10 <sup>th</sup> rad / s)	15.4421	15.4704	21.5213	15.7474	48.7771	28.9084
$E_{\kappa}$ ( $eV$ )	10.16428	10.18290	14.16571	10.36521	32.10594	19.02803
$\vec{E}_{\mu}$ (aV)	-0.2066\$	-0.20558	\$12420	-0.21333	-0.35462	-0.27301
Erm (aV)	0.17897	0,20768	0.12944	0,11159	0,40696	0.39427
F. (cV)	-0.11720	-0.10174	-0.17775	-0.15754	-0,15115	-0.07587
E. (eV)	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
( Fr (chang) (cV)	-65.77272	-65.33259	-32.74230	-67.30254	-31.78651	-31.71124
Ermy k. in ma) (aV)	-14.63489	-14.63489	-14,63489	-14.63489	-14.53414	-14,63489
Eman (4. 1) m) (eV)	٥	٥	0	0	-13.59844	-13.59844
E, (in   (eV)	7.23317	6.79303	3.47253	8,76298	3.51208	3,32988
•						

values 2	Relative	Eno
ed to the experimental	fined Experimental Relative	Total Bond Energy
able 13.288 compare	H Calculated Exper	Total Bond
energies of To	H.)	;
sition and the	HN	
nal group composition and the energies of	HN J-N-J N-J J-N J-J	;
ng file function	( - N	;
fimidazole calculated using fi	NEC	
ies of imidazol	رور	)
te total bond enem	Name	
Table 15.289.	Formula	

Exp. $\theta$	117,4 (midaxole)	136.3 (imidazole)	122.9 (imidazole)	136.3 (fmidazole)	133.2 (fmidazole)	115.8 (fmidazole)	110.4 (midazole)	138.2 (fortidazole)	129.1 (imidazəle)	106.3 (midzzale)	107.2 (fmidazole)	105.4 (imidazole)	109.8 (imidazzbi)	(111.3 (midamle)
Cal. <i>θ</i>	120.51	132.86	120,21	13.30	134.28	114.54	112.37	137.80	129.96	107.52	109.83	108.64	11.11	109.80
(©		106.63				111.18		109.83						
9 (		120.51				134.28		1(2,37						
(•) (•)														
E <sub>r</sub> (eV)	0		٥	۰	0				0	-1.44915	9038'1-	-1.85836	-1.85836	-1,44915
بز	1.00435	,	0.97435	1.07196	1,07647		59296.0		1,01912	0,82131	0,76360	0.77247	0.84958	0.82717
. دا	0.75		6.73	0.75	57.0		0.75		6.75	1	-	-	-	1
5	-		-	-	_		-		1	1	-	1	1	1
5	67.0		0.75	6.75	0.75		0.75		0.75	-	-	-	-	-
C <sub>S</sub>	0.92171 Eq.		0.82493 (Eq. (15.64))	0.86359	17716.0		0,84665 (Eq. (15.152))		0.86284 (Eq. (15.64))	0.79597	0,76360	0,77247	0.14665 (Eq. (15.152))	0,83885
ا چەرى مەسەر	0.91771		0.84665 (Eq.	0.80561	0.85252		0.87493		0.84663 (Eq. (15.151))	0.84665 (Eq. (15.152))	0,76360	0.77247	0.83252	0.81349
· Atom 2 Hybridizarion Designation	(Table 15.3R)		n	-	-		z		٥	<b>8</b> :	35	25	z	80
fication to Albert 2	-14 53414		-16.49325	.15.75493	-14.82575 .C.		-14.53414		-13.76168	-17.09334 C,	17.81791	-17.61330	-14.53414	-16,21953
Atom I Hybridization Designation	(Table 15.38)		z	22	•		•		z	z	38	13	9	c
Einstein 1	-(4,12575		-14,53414	-16,88873	15,95954		-15.95954 C.		-14,53414	-14.53414	-17,81791	.17,61330	15,95955	-16.68411
Zc' Terminal Alterns	4.0166		3,8987	4,2195	4.2740		3.8471		4,0661	4.1952	4,2426	4,3128	4,3818	4,2544
2¢' (a,)	2.59228		2.59228	2,60025	2,60925		2.59228	_	2,59228	2.60925	2.59228	2,70148	270148	2.60766
2¢,	2,01241		1.88268	2,02341	2,02241		202246		1.81258	\$2265.5	2.59228	260766	26092	2.59228
Aktas of Asplic	ZHC,"N,	ZC,C,H,	CHN,C.	,5°,5',65	,2,5,42 ZH,C,C,	ZN,C,H,	"N".5"H7	ZN,C,H,	ZHN,C,	איניני	ZC,N,C,	4C, N, C,	7K.J.'N'	ZN.C.N.

#### **PYRIDINE**

Pyridine has the formula  $C_5H_5N$  and comprises the benzene molecule with one CH group replaced by a nitrogen atom which gives rise to a C=N functional group. The aromatic C=C and C-H functional groups are equivalent to those of benzene given in the 5 Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the C=N group which is also aromatic.

As in the case of the aromatic carbons of benzene, each pyridine  $C2sp^3$  HO initially has four unpaired electrons. Each C-H bond has two paired electrons with one donated from the H AO and the other from the  $C2sp^3$  HO. In pyridine the three N2p electrons are donated to the aromatic bond. Thus, as in the case of the C=C group, each C=N bond comprises a linear combination of a factor of 0.75 of four paired electrons (three electrons) from the  $C2sp^3$  HO and the N2p AO of the participating carbon and nitrogen atoms, respectively.

The solution of the C=N functional group comprises the hybridization of the 2s and 15 2p AOs of each C to form a single  $2sp^3$  shell as an energy minimum, and the sharing of electrons between the  $C2sp^3$  HO and the nitrogen atom to form a MO permits each participating hybridized orbital to decrease in radius and energy. The C=N-bond MO is solved as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.147). The hybridization factor  $c_2(C2sp^3HO\ to\ N) = 0.91140$  (Eq. (15.116)) matches the double-bond character of the 20  $C2sp^3$  HO to the N atom, and  $C_2$  and  $C_{2o}$  in Eqs. (15.42) and (15.147) are also given by Eq. (15.116) in order to match the nitrogen to the aromatic  $C2sp^3$  HO such that  $\Delta E_{H_1MO}(AO/HO) = 0$  in Eq. (15.42). Furthermore,  $E_T(atom-atom, msp^3.AO)$  of the C=N-bond MO in Eq. (15.147) due to the charge donation from the C and N atoms to the MO is  $-1.44915\ eV$  corresponding to an energy contribution from each atom that is equivalent to that of an independent methyl group,  $-0.72457\ eV$  (Eq. (14.151)). The contributions are also the same as those for a primary amine group as given in the corresponding section. As in the case of benzene, the aromatic  $E_T(comp)$  and  $E_D(comp)$  are

given by Eqs. (15.146) and (15.147), respectively, with  $f_1 = 0.75$ . The breakage of the *CNC* bonds results in three unpaired electrons on the N atom. Thus, the corresponding  $E_{mag}$  given by Eq. (15.60) was normalized for the two bonds per atom and for  $f_1 = 0.75$  and was subtracted from the total energy of the C=N-bond MO in Eq. (15.147). The pyridine vibrational energies are similar to those of benzene [60]; thus, the value for benzene was used.

The symbols of the functional groups of pyridine are given in Table 15.291. The corresponding designation of the structure is shown in Figure 69. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), 10 (15.17-15.56), and (15.146-15.147)) parameters of pyridine are given in Tables 15.292, 15.293, and 15.294, respectively. The total energy of pyridine given in Table 15.295 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.294 corresponding to functional-group composition of the molecule. The bond angle parameters of pyridine determined using Eqs. (15.79-15.108) are given in Table 15.296.

Table 15.291. The symbols of functional groups of pyridine.

15

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH
$C_a = N$	C = N

Table 15.292. The geometrical bond parameters of pyridine and experimental values [1].	C = N $C = N $ $C = N $ $C = N $ $C = N $ $C = N $ $C = N $ $C = N $ $C = N $ $C = N $ $C = N $ $C = N $ $C = N$	1,47348 1,60061 1,47169	1.31468 1.03299 1.27073	1.39140 1.09327 1.34489	(pyridine) (pyridine) (pyridine)	0.66540 1.22265 0.74237
Table 15.292. The geometrical bond paramete	Parameter C=C Group	a (a,) 1.47348	c' (a,) 1.31468	Bond Length 2c' (A) 1.39140	Exp. Bond Length 1.394 (A)	h,c (a,) 0.66540

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Table 15.293. The MO to HO intercept ge	
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Table 15.293. The MO to HO intercept geometrical bond parameters of pyridine. $E_r$ is $E_r (a_{Inm} - a_{Iom, mnp}^2, AO)$	metrical ban	d parameters of	pyrldine. $\mathcal{E}_r$ is	$E_{\tau}(alom - alom$	, msp . AO).										
Bond .	Atom	<i>E<sub>T</sub></i> (eV) Bond I	E <sub>r</sub> (eV) Bond 2	E <sub>T</sub> (eV) Bond 3	E <sub>r</sub> (eV) Bond 4	Final Total Energy C2sp <sup>2</sup> (eV)	(°)	(a <sub>0</sub> )	Ε <sub></sub> ( <i>C2μ</i> ) (eV) (eV) Final	<i>E</i> ( <i>C2.p</i> <sup>3</sup> ) (eV) Final	. ©	6 C	(o)	(o)	(a,)
C-H (C'H)	ر".	-0.54343	-0.85035	0.36690	0	-153.57636	17716.0	0.81052	-16.78642	-16.39556	76.35	103.65	40.11	1,22423	0.19124
$C-H\left(C_{s}H\right)$	٠,٢	-0.85035	-0.85033	-0.56690	0	-(53,88327	0.91771	0.99597	-17.09334	-16.90248	74.42	105.58	38.84	1.24678	0,21379
(H)C,(H)C, = MC.	U³	-0.85035	-0.54343	-0.56690	0	-153,57636	0.91771	0.81032	25987,51-	-16.59556	128.54	51,46	53.65	0.76572	0.50501
$(H)C_{s}(H)C_{s}=NC_{s}$	2	-0,54343	-0.54343	0	0		0.93024	0.85503	15.91261		(30.6)	49.39	60.97	0.71418	0.55656
$(H)C_{s}^{N}C_{s}(H)N$	ن	-0 54343	-0.85035	-0.56690	0	-153.57636	17719.0	0.81052	-16.78542	-16.19556	134.85	45.15	19.72	0.74304	0.57165
$(H)_{C_{s}^{\infty}C_{s}}(H)_{N}$ $(H)_{C_{s}^{\infty}C_{s}}(H)_{C_{s}}(H)$	:5	-0.85035	-0.85035	0.36690	0	-153,88127	0.91771	0.79397	-17.09334	-16.90248	134,24	45.76	58.98	0.75933	0.55533

810

Table 15,294. The energy parameters (eV) of functional groups of pyridine	eV) of functional groups of	f pyridine.	
Parameters	C & C	C:H Group	C = N
λ,	0.75	-	0.75
п,	2	_	2
$n_{3}$	0	0	0
n,	0	0	0
<u> </u>	0.5	0.75	5.0
, c,	0.85252	-	0.91140
ប	1	-	_
2	0.85252	0.91771	0.91140
ប	0	-	0
c,	3	-	
ر.	0	-	0
ر:"	0.5	0.75	0.5
·: )	0.85252	_	0.91140
V, (aV)	-101.12679	-37.10024	-102.01431
V, (eV)	20.69825	13,17125	21.41410
$\Gamma\left( eV ight)$	34.31559	11.58941	34.65890
/ (cV)	-17.15779	-5.79470	-17.32945
E(+0.10) (cV)	0	-14.63489	0
Δίη, 317 (.v. m) (aV)	0	-1.13379	0
Er (m m) (cV)	0	- 01105'61-	0
$E_r(u_1w)$ (eV)	-63.27075	-31.63539	-63.27076
$E_T(atom - atom, my ^3 AO)$ (aV)	-2.26759	-0.56690	-1.44915
$E_{\tau}(\omega)$ (aV)	-65.53833	-32,20226	-64.71988
ω (10 <sup>1</sup> , rad / s)	49.7272	26.4826	43.6311
$E_{\kappa}$ (cV)	32.73133	17.43132	28.71875
$E_{D}$ ( $aV$ )	-0.35806	-0.26130	-0.33540
Exam (CV)	0.19649	0.35532 Fo (13.458)	0.19649
En (eV)	-0.25982	-0.08364	-0.23715
$E_{n_{\infty}}(\sigma V)$	0.1480.7	0.14803	0.09457
L' () (eV)	-49.54347	-32,28590	-48.82472
Bound 4. 10 10) (CV)	-14.63489	-14,63489	-14.63489
Erangle on Int) (cV)	0	-13.59844	0
Entirop (aV)	5.63881	3.90454	4,92005

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ley letter		
compared to the ex-	Relative France	-0 00073
rics of Table IS.294	Experimental Total Bond Factor	(eV) 51.87927
osition and the energ	Calculated Total Bond Energy	(5)
crional <u>proup</u> கள	N 11 5	Group
d using the fun	H.)	3
oyridine calculated	ن ۳ <del>ب</del> ن	4
e total bond energies of p	Name	ridine
Table 15.295, TI	Formula	Z Z Z

Pim Pilon and a second	ב לישו ייווניור																		
Assess of Argic 2c' 2c' 12c' 12c' 12c' 12c' 12c' 12c'	2c' Frend I (a,)	2c' lless 2 (0°)	2c' Toward Alone (a,)	F. Canadar	Atom 1 Hydridization Designation Clobe 18 181	Frank Akm 2	Atom 2 Hybridization Designation	C, Abra I	C <sub>1</sub>	r.	ů.	· ·	٧	E <sub>T</sub> (eV)	ø, ①	e ①	6. O	Cal. <i>θ</i>	Exp. θ (ο)
ZCC.C. (aromatic)	2 62936	2.62936		4,5385 -17.17218	70	.17,77218	20	0.79132	0.79232	-	-	-	0.79232	-1.85816	<del> </del>			120.19	120 [50-32] (benzene) 118.3 (pyridne)
Т. ССС.Н									$\dagger$	$\top$		1.	+		$\dagger$	$\dashv$	+	-	118.5 (pyridine)
(aromatic)														<del></del> -		120,19	=	16,911	(berzene) 121.3
ZAC.,N	2.06598	254147	3.9497	-14.82575	-	-14.53414	Z	17716.0	Eq. (15.116))	6.75	<u>-</u>	0.75	0.99312	0		-	=	17.65	115.9
ZWC.C.	2,54147	2.62936 4.5607		-14.53414	z	-16.32644 C,	13	0,91 140 Eq.	0.82377	-	-	-	0.86734	-1,44913	+	+	+	73.74	(Dyndine)
ZC.,NC.,	2.54147	2.54147	4,3359 -17,71560	-17.71560	72	-17.71360	2	+-	0.76801	<del> </del>	<del> </del>	1	100,720		$\dagger$	+	+		(pyridine)

# **PYRIMIDINE**

Pyrimidine has the formula  $C_4H_4N_2$  and comprises the pyridine molecule with one additional CH group replaced by a nitrogen atom which gives rise to a second C=N functional group that is equivalent to that of pyridine given in the corresponding section. The 5 aromatic C=C and C-H functional groups are also equivalent to those of pyridine and benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the C=N group which is also aromatic.

The symbols of the functional groups of pyrimidine are given in Table 15.297. The corresponding designation of the structure is shown in Figure 70. The geometrical (Eqs. 10 (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyrimidine are given in Tables 15.298, 15.299, and 15.300, respectively. The total energy of pyrimidine given in Table 15.301 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.300 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrimidine determined using Eqs. (15.79-15.108) are given in Table 15.302.

Table 15.297. The symbols of functional groups of pyrimidine.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH
$C_{a,b,d} = N$	C = N

نے	Ç Ømin	1.47169	1.27073	489	40 idine)	237	
perimental values [1]	γ <sub>a</sub> ς Seign	1.47	1.27	1.34489	1.340 (pyrimidine)	0,74237	
of pyrimidine and exp	C.H. Group	1,60061	1.03299	1.09327	1.084 (pyridine)	1,22265	063539
Table 15.298. The geometrical bond parameters of pyrimidine and experimental values [1].	C=C Group	1.47348	1.31468	1.39140	1.393 (pyrimidine)	0.66540	0.89223
Table 15.298. The geon	· Parameter	0 (0,)	c' (a <sub>0</sub> )	Bond Length 2c' (A)	Exp. Bond Length (A)	h,c (a,)	,

oud pa	ne. $E_T$ is $E_T(atann - atom, msp^2, AO)$ .	· atom, msp². AO).											
Atom $E_T$ $E_T$ $E_T$ $E_T$ (eV) (eV) (eV)			E. E.	Final Total Encrgy	Jones I	30	("445)"	$E(C2sp^{J})$	.0	9	ι <sub>θ</sub>	9	ď
Bond 2			Bond 4	(2.sp3	(%)	(°)	Final	Final S	©	© 	© 	(a.)	(%)
C0 54343 -0 54143 -0 5650			0	-153.26945	17719.0	0.12562	-16.47951	-16.28864	78.27	101.73	41.39	1,20084	0.16745
(', -0.34343 -0.83035 -0.86500			0	-153.57636	0.91771	0.81052	-16 78642	-16,59556	76.35	103.65	40.11	1,243	0.19124
C; -0.85035 -0.85035 -0.36690			0	-(53.88327	0.91771	0.79597	-17.09334	-16.90248	74.42	105.58	38.84	1,24678	0.21379
C, -0.83033 -0.54343 -0.56690			0	9692561-	0.91771	0.81052	-16,78642	-16.59556	128.54	51.46	31.63	0.76572	0.50501
N <sub>A</sub> -0.54343 -0.54343 0			0		0.93084	0.85503	-15.91261		130.61	49.39	60.97	0.71418	814
(,, -0.5434) -0.5689			o	-153,26945	0.91771	0,82562	-16,47951	-16.28865	129.26	50.74	59.44	0.74824	0.52249
N <sub>A</sub> -0.54343 -0.54343 0			c		0.93084	0.85503	-15.91261		13061	49.39	60.97	0.71418	0.55656
0.15015 -0.15015 -0.50650	•		o	-(53.88327	17710.0	0.79597	-17.09334	-16.90248	134.24	45.76	58.98	0,75935	0.55533
-0.85035 -0.543430.55690			0	-153,57636	17716.0	0.81052	-16.78642	-16.39556	134.85	43.15	59.72	0.74304	0.57165

Table 15,300. The energy parameters (eV) of functional groups of pyrimidine.	:V) of functional groups of p	syrinidine,	
Parameters	2#2 2#2	C:H Group	ر ر ا بر ر س
<i>J</i> <sup>1</sup>	0.75	-	0.75
-	2	-	2
£ .	o	0	0
ដ៍	0	O	0
5	0.5	0.75	5.0
$c_i$	0.85252	1	0.91140
5	1		1
c,	0.85252	0.91771	0.91140
( 5,	0	1	0
6,	3	1	3
6	0	1.	0
7.,1	0.5	0.75	0.5
ن	0.85252	_	0.91140
V, (eV)	-101,12679	-37,10024	-102,01431
V, (eV)	20.69825	13.17125	21.41410
7 (01/)	34.31559	11.58941	34.65890
V (cV)	-17.15779	-5.79470	-17.32945
E(.c) no) (eV)	0	-14.63489	0
AF no wo (cV)	0	-1.13379	0
Er (20-10) (cV)	0	-13.50110	0
F, (w, n) (aV)	-63.27075	-31.63539	-63.27076
$E_T \left( alnm - alom, nixp^3 . AO \right) (aV)$	-2.26759	-0.56690	-1,44915
5. (va) (0V)	-65.53833	-32.20226	-64.71988
ω (10 <sup>13</sup> rad I.s.)	49.7272	26.4826	43.6311
$E_{K}(eV)$	32.73133	17.43132	28.71875
$\vec{E}_n$ (eV)	-0.35806	-0.26130	-0.33540
ligate (aV)	0.19649	0.35532 En (13 458)	0.19649
F. (aV)	-0.25982	-0.08364	-0.23715
$\mathcal{E}_{\alpha,\alpha}\left(\sigma^{\mathcal{V}}\right)$	0.14803	0.14803	0.09457
Fy (comp) (CV)	-49.54347	-32.28590	-48.82472
Franch (1, so mu) (eV)	-14.63489	-14.63489	-14.63489
Em (a. 10 m) (aV)	0	-13.59844	0
$E_{ij}$ (complete)	5.63881	3,90454	4.92005

the experimental values [2]. ].	
00 compared to	Relative Error
nergies of Table 15.3	Experimental Total Bond Energy
composition and the c	Calculated Total Bond Energy
unctional group a	
Aled using the (	н.)
s of pyrimidine calcul	ري.
he total bond energie	Name
1 able 15.301. 7	Formula

Table 15.302. The bond engle parameters of pyrimidine and experimental va-	gle paramet	ers of pyri	midine an	d experimen	tel values [1]. Er	is Er(ann -	alues [1]. $E_r$ is $E_r$ (atom - atom, $m_s p^3$ , $AO$ ).												
Absax (d'Arga	2¢'  head 1   (a,)	2¢' lend2 (o,)	2c' Terminal Alexus (a <sub>n</sub> )	E. Ains f	Atom ( Hydridization Destgnation (Table 15.3B)	Et.	Atom 2 Hybridization Designation (Table 15.3B)	S <sub>1</sub>	C <sub>1</sub>	C-	ď	. 5	25	£ <sub>r</sub> (e.v)	ø, 🗇	0 0	e 🖭	Cel.	Exp. θ (°)
AT:(' (aromatic)	1,62936	7,62936	45365	-(7,17218		-17.17218	70	0.79232	0.79232	-	-	-	0.79132	-1.63836		<del> </del>	<del> </del>	61.021	(20 (30-52) (benzens) (18.3 (pyridins) 118.5
AXX'H (eromatic)																61.051		119.91	(bynans) (20 (30-52) (benzene) (21.3)
ZHCN	2,0659\$	2.0639\$ 2.54147 3.9497	3.9497	-14.82575	~	-14.53414	z	17716	0.9(140 Eq.	0.75	-	0.75	0.99312	0	1	+	+	117.65	(pyridine) 115.9 (byridine)
ZNC:C	2,54147	2.62936	4,5607	-14.53414	z	-16.52644	n	0.91140 Eq.	2777	-	-	·-	0.86734	-1.44915	$\vdash$	<del> </del>		123.76	123.9 (byridne)
לכאל.	2,54147	2,54(47	43359	-17.71560	2	-17.71560	×	0.76801	0.76801	-	-	-	0.76801	-1.85836	T	$\dagger$	$\dagger$	178	115.5
ZNC.N	254147	2,54147		4.5826 -15.55033	r	-(5.55033	•	0.87495	0.87495	-	-	-	0.87495	-1.85816	$\dagger$	+		17.871	(pyrimidina) 127.6

#### **PYRAZINE**

Pyrazine has the formula  $C_4H_4N_2$  and comprises the pyrimidine molecule with para rather than ortho aromatic nitrogen atoms. The C=N functional group is equivalent to that of pyrimidine and pyridine given in the corresponding sections. The aromatic C=C and C-H functional groups are also equivalent to those of pyrimidine, pyridine, and benzene given in the Aromatic and Heterocyclic Compounds section with the aromaticity maintained by the electrons from nitrogen in the C=N group which is also aromatic.

The symbols of the functional groups of pyrazine are given in Table 15.303. The corresponding designation of the structure is shown in Figure 71. The geometrical (Eqs. 10 (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of pyrazine are given in Tables 15.304, 15.305, and 15.306, respectively. The total energy of pyrazine given in Table 15.307 was calculated as the sum over the integer multiple of each  $E_D(croup)$  of Table 15.306 corresponding to functional-group composition of the molecule. The bond angle parameters of pyrazine determined using Eqs. (15.79-15.108) are given in Table 15.308.

Table 15.303. The symbols of functional groups of pyrazine.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	СН
$C_a = N$	C = N

							_
I values !!	Croup Group	1.47169	1.27073	1.34489	1.403 (pyrazine)	0,74237	0.86345
pyrazine and experimenta	CH	1.60061	1,03299	1.09327	1,115 (pyrazine)	1,22265	0.64537
T-11- 14 104 The recometrical bond parameters of pyrazine and experimental values [1]	C. C. C. C. C. C. C. C. C. C. C. C. C. C	1,47348	131468	1,39140	1,339 (pyrazine)	0.66540	0.89223
Table 15 104 The Water	Parameter	0 (0,)	c. (a,)	Bond Leugh 2c' (A)	Exp. Bond Length	h,c (a,)	1

Table 15,305. The MO to HO intercept geometrical bond parameters of pyrazine.	netrical bon	d parameters of	pyrazine. E <sub>7</sub> 13	Er is Er (dram - diam, misp . AC).	. msp . Ac. j.					1	ľ	-	٩	-	P
Bond	Atom	E <sub>r</sub> (eV)	E <sub>T</sub> (eV) Bond 2	(eV) Bond 3	E <sub>7</sub> (eV) Bond 4	Final Total Energy C2xp*	] &	(°)	Er(C2rp') (eV) Final	E(CLsp²) (eV) Final	. C	ō (C)	. O	. (°)	r (g
						(eV)								100	0.10174
	,		320340	08998 0	٥	-153.57636	17716.0	0,81052	-16.78642	-16.59556	76.35	103.65	401	Charle	
(H (C,H)	٠	Cache.										77.53	27 63	CL 245.0	0.50501
2	ر	-0.83035	-0,54343	0.56690	٥	-153,57636	17716.0	0.81052	-16.78642	-16,59536	128.34	31.40	60.00		
$(H)C_{\bullet}(H)C_{\bullet}=NC_{\bullet}$	;												50 67	0.71718	25,955.0
3	2	-0.54343	-0.54343	•	•		0.93084	0.85503	-15.91261		19:051	49,19	16,00	,	
(H)C,(H)C,=NC,	:										20000		6.7	0 24304	0.57763
1 (11) 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	ü	-0.85035	-0.54343	0.56690	•	-153.57636	17716.0	0.81052	-16.78642	-16.39336	134.85	1			
N(U), = , J(U)N															

Table 15.306. The energy parameters (eV) of functional groups of pyrazine.	eV) of functional groups of	pyrazine.	
Parameters	<u>ا</u> د د د د د د د د د د د د د د د د د د د	CH Group	C= N
y	0.75	-	0.75
4	-		,
	•		•
	,		
",	0	۵	0
ن	5'0	0.75	0.5
Ç.	0.85252	1	0,91140
د'		1	1
c,	0.85252	0.91771	0,91140
5	0	. 1	0
ر*	3	1	£
62	0	-	0
( C.	0.5	6.75	0.5
<i>C</i> <sub>2</sub> ,	0.85252	1	0.91140
V, (eV)	-101.12679	-37.10024	-102.01431
V, (eV)	20.69825	13,17125	21.41410
T (aV)	34,31559	11.58941	34.65890
V_ (eV)	-17.15779	-5.79470	-17.32945
E[w m) (aV)	0	-14.63489	0
DEning (w m) (eV)	0	-1.13379	0
(Sr (no no) (aV)	0	-13.50110	D
$E_r(u, \iota \sigma)$ (cV)	-63.27075	-31.63539	-63.21076
$E_T(atom - atom, msp^3, AO)$ (4V)	-2.26759	06995'0-	-1.44915
$E_{\mathbf{r}}(\mathbf{x}\mathbf{r})$ (aV)	-65.53833	-32.202.26-	-64.71988
(10" rad /.x)	49.7272	26,4826	43,6311
$E_{\mathcal{F}}(cV)$	32,73133	17,43132	28.71875
E, (cV)	-0.35806	-0.26130	-0.33540
$\widehat{E}_{ m fred}$ (aV)	0.19649	0.35532 Eq. (13.458)	0.19649
E., (aV)	-0.25982	-0.08364	-0.23715
Em (aV)	0.14803	0.14803	0.09457
E, from, (cV)	-49.54347	-32.28590	-48.82472
Einne (r, write) (cV)	-14,63489	-14.63489	-14.63489
Guma (c. so in) (aV)	0	-13.59844	0
Entimes (CV)	5.63881	3.90454	4.92005

e experimental values [2] 1	1111
connared to the	Refative Error
ergies of Table 15.306 cor	Experimental Total Bond Energy
mposition and the ene	Calculated Total Bond Energy
ictional group co	Ç. Spen
led using the fur	CH
yrazme calcula	ں ن
the total bond energies of b	Name
יותרים	Formula

	-									į									
$ \begin{pmatrix} z_1 & z_2 & z_3 & z_4 & z_4 \\ Und 1 & Und 2 & Termin \\ (a_1) & (a_2) & Termin \\ & & & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & &$	; <u>[</u> 6	(°a)	Trummed Altumed (a <sub>6</sub> )	A Line	Atom I Hybridization Designation (Table 15.38)	Aim 2	Atom 2 Hybridization Designation (Table 18 18)	C <sub>2</sub>	C <sub>2</sub>	່ບ			`&	E <sub>r</sub> (eV)	ø, ©	6-0	e.⊙	Cal. 9	Exp. 8
ZCCC (aromatic)	2,62936	2.62936	4.5585	81221.71-	R	-17,17218	20	0.79232	0.79232	-	-	-	0.79232	-1.85836				120.19	120 [50-52] (benzene) 118.3 (pyridine)
7.7.7																	_		(byddina)
(aromatic)																120.19	<u> </u>	16.911	120 (30-52 (benzeno)
14.317									001140									_	(57) (57)
V 707	4.00394	734167	3.9497	-14.82575	_	-14.53414	z	0,91771	븁	0.73	-	0.75	0.99312	•			_	- 17	115.9
ACCH.									(13.116))	1								60'/ 11	(pyridine)
				1		1						_				17.65	116.81	125.54	123.9
ZWCC.	2.54147	2.62936	4,4045	-14.53414	z	-17.09334		0.91140 Eq.	0.79597	_	_	-	0.85368	-1.44915	T	+-	┿	, , , , , , , , , , , , , , , , , , ,	(pyrazine) 115.6
:X.XC	2,54147	2.54147	43359	-(771560	7			STEE STEE STEE STEE STEE STEE STEE STEE	1							_	_		(pyrazine
			٦.		:	-17.71500	<b>1</b> 7	0.76801	0.76801	-	_	<u>-</u>	0.76801	AFRIA.	-		ŀ		116.8

## **QUINOLINE**

Quinoline has the formula  $C_9H_7N$  and comprises the naphthalene molecule with one CH group replaced by a nitrogen atom which gives rise to a C=N functional group. The aromatic C=C and C-H functional groups are equivalent to those of naphthalene given in the corresponding section with the aromaticity maintained by the electrons from nitrogen in the C=N group which is also aromatic. The C-C functional group is also equivalent to that of naphthalene. The bonding in quinoline can be further considered as a linear combination of the naphthalene and pyridine groups wherein the C=N group is equivalent to that of pyridine, pyrimidine, and pyrazine as given in the corresponding sections.

The symbols of the functional groups of quinoline are given in Table 15.309. The corresponding designation of the structure is shown in Figure 72. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of quinoline are given in Tables 15.310, 15.311, and 15.312, respectively. The total energy of quinoline given in Table 15.313 was calculated as the sum over the integer multiple of each  $E_D(Group)$  of Table 15.312 corresponding to functional-group composition of the molecule. The bond angle parameters of quinoline determined using Eqs. (15.79-15.108) are given in Table 15.314.

Table 15.309. The symbols of functional groups of quinoline.

Functional Group	Group Symbol						
CC (aromatic bond)	C = C						
CH (aromatic)	СН						
$C_b - C_b$ (bridging bond)	C-C						
$C_{a,d} = N$	C=N						

	C=N Oroup	1,47169	1.27073	1,34489	1.340 (pyridine)	0.74237	0.86345
ital values [1]	C – C Group	1.75607	1.32517	1.40250	1.42 (naphthalene)	1.15226	0.75462
quinoline and experimen	C:H Group	1.60061	1.03299	1.09327	1.101 (benzeno)	1.22265	0.64537
rical bond parameters of	5. C=C Group	1,47348	1,31468	1,39140	1.40 (avg.) (naphthalene)	0.66540	0.89223
Table 15.310. The geometrical bond parameters of quinoline and experimental values [1].	Parameter	(°0) 0	د. (۵۰)	Bond Length 2c' (A)	Exp. Bond Length (A)	h,c (o <sub>0</sub> )	

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16	)78	8								8:	22_				
			( g	(•)	0.19124	0.21379	0.57165	0.55533	\$5075.0	0.58725	0.5050	0.55636	0.52113	0.07066	0.09061
			(a)	(*)	1.22423	1.24678	0,74304	0.75935	0.74430	0.72743	0.76572	0.71418	0.74960	1,25451	1.23456
			, (o	>	40.11	38.84	59.72	58.98	39.68	60.42	53.65	76'09	86.68	44,41	45,33
			o @	2	103.65	105.58	45.15	45.76	45.19	44.58	51.46	4939	50.79	84.99	13.69
			. <sub>0</sub> ©	>	76.35	74.42	134,85	134.24	134,81	135.42	128.54	130.61	123.21	10'86	16.39
			E(C2sp²)	Final	-16.59556	-16.9024\$	95565'91-	-16,90248	-16,61903	1121891-	95565.91-		-1631211	16,61903	-16.31211
			(eV)	Final	-16.78642	-(7.09334	-16,78642	-17.09334	-16.80989	86205,61-	-16,78642	-13.91261	-16.30297	-16.80989	.16 50298
			13	(%)	0.81052	0.79597	0.81052	0,79597	0.80939	0.82445	0 \$1052	0.85503	0.82443	0.80939	0.82445
			13	(*)	17716.0	17716.0	17716.0	17716.0	17716.0	17719.0	0.91771	0.93014	17116.0	17716.0	17716.0
			Final Total Energy	(eV)	-153.57636	-153.86327	-153.57636	-153,88327	-153.59983	26252'551"	-153,57636		183,29291	153,59983	-153,29292
0.74237	0.86345	т,тхр³.40).	(eV)	Bond 4		0	o	0	0	0	0	0	0	0	•
1.15226	0.75462	$E_{ au}$ is $E_{ au}ig(aom-aom,msp^3.AOig)$	(eV)	Bond 3	-0.36690	-0.56690	-0.36650	-0.56690	-0.28345	-0.28345	-0.56690		-0,28345	-0.28345	-0 28345
-	7.0		E <sub>7</sub>	Bond 2	-0.54343	-0.15035	-0.54343	-0,85035	-0.83033	-0.54343	-0.54343	0.54343	-0.54343	-0.83035	-0.54343
1.22265	0.64537	parameters of q	(e, t,	Bond i	-0.85035	-0.85035	-0.85033	-0.85035	-0.85035	-0.BSØ3S	-0.85035	-0.54343	-0.85035	-0 \$5035	-0 15035
_		etrical bond	Atom		ن'	ับ	.,	ن'	ن	ű	C,	*	ŭ	ú,	3
0.66540	0.89223	HO intercept geom													
h,c (0,)	9	Table 15311. The MO to HO intercept geometrical bond parameters of quinoline.	Bond		C-H (C,H)	$C - H \left( C_{\mu} H \right)$	$N(H)C_s = C_s(H)$	$(H)C_{i}^{\lambda}=C_{i,\lambda,i,J}(H)$	(H)C,(C,)C,=C,	N(C,)C, =C,	$C_{\mu}(H)C_{\mu}=N$	$C_{\kappa}(H)C_{s} = N$ $C_{\kappa}(C_{s})C_{s} = N$	C, (C, )C, = N	$(H)C_i \stackrel{N}{=} C_i - C_j$	N(C,)C,-C,
	Ц	F	<u>e</u>		۷	۲	لکا	لثا	ت			U U	ان	$\stackrel{\cdot}{=}$	^

Table 15,312. The energy parameters (6V) of functional groups of quinoline.	V) of functional groups of	quinoline.		
Parameters	Sign Caron	C.H Group	C-C Group	≥ noi S O O
γ.	0.75			0.75
n,	7			2
",	0		0	0
n,	0	0	0	0
כ'	0.5	0.75	0.5	0.5
<i>C</i> ,	0.85252	1	1	0.91140
, c,	1	-	1	~
c,	0.85252	0.91771	0.85252	0.91140
5	0	1	0	0
, c <sub>4</sub>	3	_	2	3
C <sub>3</sub>	0	_	0	0
ر؛•	0.5	0.75	6.5	0.5
<u> </u>	0.85252	_	-	0,91140
V, (aV)	-101.12679	-37,10024	-34.43791	-102.01431
V, (eV)	20.69825	13.17125	10.26723	21,41410
T (eV)	34,31559	11.58941	9.80539	34.65890
V., (eV)	-17.15779	-5.79470	4.90270	-17.32945
E(n m) (eV)	0	-14.63489	-14.63489	0
DE u, so (in in) (aV)	0	-1.13379	-1.13379	0
15 (w m) (cV)	0	-13.50110	-13.50110	0
$E_r(n_s \omega)$ (eV)	-63.27075	-31.63539	-31.63529	-63.27076
$E_r(alom - alom, insp^2, AO)$ (eV)	-2.26739	-0.56690	06995"0-	-1.44915
Er (10) (aV)	-65,53833	-32,20226	-32.20226	-64.71988
ω (1013 rad I.S)	49,727.2	26.4826	23.6343	43.6311
$E_{K}$ (eV)	32.73133	17.43132	15.55648	28.71875
$\vec{E}_n(eV)$	-0.35806	-0.26130	-0.25127	-0.33540
E 44 (aV)	0.19649	0.35532 Eq. (13.458)	0.12312	0.19649
E. (aV)	-0.25982	-0.08364	-0.18971	-0.23715
$E_{m_{eff}}\left( eV ight)$	0.14803	0.14803	0.14803	0.09457
$E_T^{(i_1,, i_r)}(aV)$	-49,54347	-32,28590	-32.39198	48.82472
Emma(r, an ind) (cV)	-14.63489	-14.63489	-14.63489	-14.63489
Emay (a.10 10) (UV)	0	-13.59844	0	0
En (tomp) (aV)	5.63881	3.90454	3.12220	4.92005

	Cal. 6		119.40		120.30
	e, €	:			
	6 0	:		9, 91,	2
	ø, 🖸			ļ	
	E, (eV)		-1.85836		
	У		0.79232		
nes [2]. J	5		-		
Relative Error	ບ້		-		
ital nargy Re	ڻ				-
Confidence to the Confidence of the Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confidence of Confiden	C <sub>1</sub>		0.79232 0.79232		0.78050 0.76801
Calculated Total Band Energy (e.V) 85,40453	C, Aber I		0.79232		0.78050
V         Total foundation           V         Total foundation           P         Total foundation           P         (eV)           (eV)         (eV)           10         (eV)           10         (eV)           10         (eV)           10         (eV)           10         (eV)           10         (eV)	Atom 2 Hybridization Designation	(Table (3.3B)	3		7.
$C = N$ Group $2$ $2$ $C_{\tau}(aton - aton$	Eradente Aton: 2	10.101			-17.71560
C-(' Group 1 1 1 values [1]. E, is ,	Atom I Hybridization Designation	╁		1	22
CH 7 experiment	Eradon A	-17.17218			-17.43216
C=C	. 2c' Temand Alama (a,)	4.3585			4.3818
rs of quin	2c' Bendi (a,)	2,65034		1	734147
Name 1816 parameter	2c' Nand 1 (a,)	262936 265034 4,3585		15157	4.3818
Ouinbine 14. The bond at		70,07	H.J.Z	7C NC	
Pormula C,H,N Table 15.3					

### ISOQUINOLINE

Isoquinoline has the formula  $C_9H_7N$  and comprises the naphthalene molecule with one CH group replaced by a nitrogen atom which gives rise to a C=N functional group. Isoquinoline is also equivalent to quinoline with the nitrogen in the meta rather than the ortho position relative to the benzene ring of the molecule. The aromatic C=C and C-H functional groups are equivalent to those of naphthalene given in the corresponding section with the aromaticity maintained by the electrons from nitrogen in the C=N group which is also aromatic. The C-C functional group is also equivalent to that of naphthalene. The bonding in isoquinoline can be further considered as a linear combination of the naphthalene and pyridine groups wherein the C=N group is equivalent to that of pyridine, pyrimidine, pyrazine, and quinoline as given in the corresponding sections.

The symbols of the functional groups of isoquinoline are given in Table 15.315. The corresponding designation of the structure is shown in Figure 73. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11), (15.17-15.56), and (15.146-15.147)) parameters of isoquinoline are given in Tables 15.316, 15:317, and 15.318, respectively. The total energy of isoquinoline given in Table 15.319 was calculated as the sum over the integer multiple of each  $E_D(G_{Dusp})$  of Table 15.318 corresponding to functional-group composition of the molecule. The bond angle parameters of isoquinoline determined using Eqs. (15.79-15.108) are given in Table 15.320.

Table 15.315. The symbols of functional groups of isoquinoline.

Functional Group	Group Symbol
CC (aromatic bond)	C=C
CH (aromatic)	СН
$C_b - C_b$ (bridging bond)	C-C
$C_{a,d} \stackrel{3\epsilon}{=} N$	C = N

			_				_
	ريد Grænp	1.47169	1.27073	1.34489	1.340 (pyridine)	0.74237	0.86345
ntal values [1].	C-C Group	1.75607	1.32517	1,40250	1.42 (naphtitalene)	1.15226	0.75462
Table 15.316. The geometrical bond parameters of isoquinoline and experimental values [1]	CH Group	190091	1.03299	1.09327	1.101 (benzene)	1,22265	0.64537
	C≒C Group	1,47348	1.31468	1,39140	1.40 (avg.) (naphthalene)	0,66540	0.89223
Table 15.316. The geom	Parameter	a (a,)	c. (a,)	Bond Length 2c' (A)	Exp. Bond Length (A)	h,c (v <sub>0</sub> )	o

Table 15.317. The MO to HO intercept geometrical bond parameters of isoquinoline.	etrical bond	parameters of it		E, is E, (atom - atom, msp AO)	tom,msp AO).	•										
	Atom	E, (cV)	E <sub>T</sub> (eV) Bond 2	E <sub>7</sub> (eV) Bond 3	E <sub>T</sub> (eV) Bond 4	Final Total Energy C2xp³ (eV)	,} <u>e</u>	'3 (°a)	Ec(Cip') (cV) Final	E(C2sp²) (eV) Pinal	.e ©	- <mark>'</mark> -(€)	6.0	(°)	(°p)	
C-H (C,H)	U)	-0.83035	-0.54343	-0.36690	0	-153,57636	17719.0	0.81052	-16.78643	-16.59556	76.35	103.65	40.11	1,23423	0.19124	
(. – H (C,H)	C,	-0.55035	-0.54343	-0.56690	0	-153.57636	17710.0	0.81052	-16.78642	-16.59556	76.35	. 103.65	40.11	1,23423	0,19124	
כ-	ر'	-0.85035	-0.85035	-0.56690	0	-153.88327	17716.0	0.79597	-17,09334	-16.90248	74.42	105.58	38.14	1.34678	0.21379	
N(H)c,=C, N(H)c,=C,	ປ່ ປ	-0.85033	-0.54343	-0.36690	0	-153,57636	177160	0.81052	-16,78642	-16.59556	134.85	45.15	18.n	0.74304	0.57165	
$(H)_{C_{\rho}} \stackrel{\lambda}{=}_{C_{\rho_{\rho},\rho}}(H)$	,	-0 85035	-0.85035	06995'0-	0	153.88327	12719.0	0,79397	-17,09334	-16.90248	134,24	45.76	58.93	0.75935	0.55533	82
H)C, (C,) C,=C,	۲,	-0.83033	-0.83015	-0.28345	0	-133.19983	0.91771	0.80939	-16.80589	-16,61903	134,81	45.19	29.66	0.74430	0.57038	6 _
$C_{r}(H)C_{s}^{-1}N$ $C_{r}(H)C_{s}^{-1}N$	ڻ' <del>'</del> ن	-0.85035	-0,54343	· -0.56670	0	-153.57636	0.91771	25018:0	-16.78642	.16.59536	128.54	51.46	58.65	0.76572	0.50501	
$C_r(H)C_s^{\frac{2r}{2r}}$ $C_r(H)C_s^{\frac{2r}{2r}}$	X	-0.54343	-0.54343		0		0 93084	0 85503	-15.91261		130.61	49.39	76'09	0,71418	0.55656	
,,(c,)c,-c,	ر: ً	-0.85035	-0.85035	-0.28345	0	-153,59983	17716.0	0.80939	-16.80929	-16.61903	93.01	84.99	44.41	1.25451	99010 0	

ζ'	Godin C	Group	Group	Group
	0,75	-	-	0.75
, n	2	_	-	2
$n_{\mathbf{i}}$	0	0	C	0
ŭ	0	0	0	٥
. c.	0.5	0.75	0.5	0.5
ر:	0.85252	-	ı	0.91140
ъ	-	-	1	-
5	0.85252	0.91771	0.85252	0,91140
5	0	-	0	0
6,	3		2	3
C,	0	-	0	0
 	0.5	0.75	0.5	0.5
C;	0.85252	1	-	0.91140
V, (cV)	-101,12679	-37.10024	-34.43791	-102.01431
V, (eV)	20.69825	13,17125	10.26723	21.41410
7 (eV)	34,31559	11.58941	9.80539	34.65890
V. (cV)	-17.15779	-5.79470	-4,90270	-17.32945
$E(\sigma m) (uV)$	0	-14.63489	-14,63489	0
δΕ m, 14, (40 m) (4V)	0	-1.13379	-1.13379	0
$E_{r}(n m) (cV)$	0	-13,50110	-13.50110	0
E. (11,20) (cV)	-63.27075	-31.63539	-31.63529	-63.27076
$E_r(atom - atom, msp^*, AO)$ (cV)	-2.26759	-0.56690	-0.56690	-1.44915
$E_r(\iota, \sigma)$ (eV)	-65.53833	-32,20226	-32.20226	-64.71988
ω (1013 rad/x)	49.7272	26,4826	23.6343	43.6311
$E_{\chi^{*}}(eV)$	32,73133	17.43132	15.55648	28.71875
$ec{E}_{_{\mathrm{D}}}$ (aV)	-0,35806	-0.26130	-0.25127	-0.33540
Exit (aV)	0.19649	0.35532 Eq. (13.458)	0.12312	0.19649
E (cV)	-0.25982	-0.08364	-0.18971	-0.23715
$E_{m_{\mathbf{w}}}(aV)$	0.14803	0.14803	0.14803	0.09457
Er (13-4) (aV)	-49,54347	-32.28590	-32,39198	-48.82472
E (4. 40 HO)	-14.63489	-14.63489	-14,63489	-14.63489
Eman (c. 10 m) (cV)	0	-13.59844	0	0
En (comp) (aV)	5.63881	3.90454	3.12220	4,92005

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Formule Na		C.H.N Isoquinoline		Table 15 320. The band angle parameters of isoquinoline and experimental values [1]. $t_r$ is $t_r$ (atom – atom, may $a \cap f$ ).		Akara of Angla		_		- - - - -	17.7.77		
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#### INDOLE

Indole having the formula  $C_{\rm g}H_{\gamma}N$  comprises a phenyl moiety with a conjugated five-membered ring which comprises pyrrole except that one of the double bonds is part of the aromatic ring. The structure is shown in Figure. 74. The aromatic  $C_{=}^{3e}C$  and C-H functional groups of the phenyl moiety are equivalent to those of benzene given in the Aromatic and Heterocyclic Compounds section. The CH, NH, and  $C_{d}=C_{e}$  groups of the pyrrole-type ring are equivalent to the corresponding groups of pyrrole, furan, and thiophene where present as given in the corresponding sections. The  $C_{b}-C_{d}$  single bond of aryl carbon to the  $C_{d}=C_{e}$  bond is also a functional group. This group is equivalent to the C-C(O) group of benzoic acids with regard to  $\Delta E_{H,MO}(AO/HO)$  in Eq. (15.42) and  $E_{T}(atom-atom,msp^{3}.AO)$  in Eq. (15.52) both being -1.29147 eV. This energy is a linear combination of  $\frac{-1.13379 \text{ eV}}{2}$ ,  $E_{T}(atom-atom,msp^{3}.AO)$  of the C-H group that the  $C_{b}-C_{d}$  and C-C(O) groups replace, and that of an independent  $C2sp^{3}$  HO, -0.72457 eV (Eq. (14.151)). However, as in the case of pyrrole, the indole hybridization term  $c_{2}$  is the 15 aromatic  $c_{2}(benzeneC2sp^{3}HO)=0.85252$  to match the aryl  $C2sp^{3}$  HO, and the energy terms corresponding to oscillation in the transition state correspond to indole.

As in the case of pyrrole, the C-N-C-bond MO comprising a linear combination of two single bonds is solved in the same manner as a double bond with  $n_1 = 2$  in Eqs. (15.42) and (15.52). The hybridization factor  $c_2(arylC2sp^3HO\ to\ N) = 0.84665$  (Eq. 20 (15.152)) matches the aromatic character of the  $C2sp^3$  HOs to the N atom of the NH group, and  $C_2$  and  $C_{2n}$  in Eqs. (15.42) and (15.52) become that of benzene given by Eq. (15.143),  $C_2(benzeneC2sp^3HO) = 0.85252$ . Furthermore,  $\Delta E_{H,MO}(AO/HO)$  in Eq. (15.42) and  $E_T(atom-atom,msp^3.AO)$  in Eq. (15.52) are both  $-2.42526\ eV$  which is a linear combination of  $\frac{-1.13379\ eV}{2}$ ,  $E_T(atom-atom,msp^3.AO)$  of the C-H group that the 25  $C_c-N$  bond replaces, and  $-1.85836\ eV$  (Eq. (14.513)) which is equivalent to the corresponding component of the C-N-C-bond of pyrrole.

The symbols of the functional groups of indole are given in Table 15.321. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of indole are given in Tables 15.322, 15.323, and 15.324, respectively. The total energy of indole given in Table 15.325 was calculated as the sum over the integer multiple of each  $E_D(G_{PRUP})$  of Table 15.324 corresponding to functional-group composition of the molecule. The bond angle parameters of indole determined using Eqs. (15.79-15.108) are given in Table 15.326.

Table 15.321. The symbols of functional groups of indole.

Functional Group	Group Symbol
CC (aromatic bond)	C = C
CH (aromatic)	CH (i)
$C_d = C_e$ double bond	C = C
$C_h - C_d$	C – C
CH	CH (ii)
$C_c - N - C_e$	C-N-C
NH group	<i>NH</i>

Table 15.322, The	able 15.322. The geometrical bond parameters of indole and experimental values [1]	reters of indole and exper	incental values [1].					
Parameter	C=C Group	C.H. (i) Group	C≈C Group	C'H (ii) Group	C~C Group	C-N-C Group	<i>NH</i> Group	
a (a <sub>o</sub> )	1.47348	19009'1	1.45103	1.53380	1,81395	1,44394	1.24428	
c' (a,)	1.31468	1.03299	1,30463	1.01120	1,34683	1,30144	0.94134	
Bond Length 2c' (A)	1.39140	1,09327	1,38076	1.07021	1,42542	1.37738	0.996270	
Exp. Bond Length (A)	1.399 (benzene)	1.101 (benzene)	1.382 (pymole)	1.076 (pyrrole	1.417 (pyrrole)	1.370 (рупоlе)	0.996 (pymale)	
h,c (a,)	0.66540	1,22265	0.63517	1.15326	1,21510	0.62548	0.81370	
25	0.89223	0.64537	01668'0	0.65928	0.74248	0.90131	0.75653	

0.8922.3	0.04337	760	0.67910	0.0	0.007.00	0,74740		0.701.51	1	0.7.003						
Table 15.323. The MO to HO intercept geometrical bond parameters of indole. $R_1$ is	edmetrical bor	nd parancters of		an alkyl group and $R_iR_i^*R^*$ are $H$ or alkyl groups. $E_r$ is $G_rig(alom-alom,msp^2,AOig)$	R.R.R. are H	or alkyl group	18. Er is Gr (4	טוח מוחח מוחח	sp. 40).							
Bond	Atom	Er	li,	. E <sub>T</sub>	Er	Final Total	7.	رالم	F(G2m')	E(C25p")	je,	9	e,	d,	d,	
		(cV) Bond I	(eV) Bond 2	(eV) Bond 3	(eV) Bond 4	('2xp')	(°)	(%)	Final	(eV) Final	©	©	©	(%)	(°)	
(-H (C,H)	٠	-0.85035	-0.85035	0.36690	0	-153,88327	0.91771	0,79397	-17.09334	-16.90248	74.42	105.58	38.64	1.24678	0,21379	
(', = H(', = (',	ڻ	-0.85035	2 8 2 0 3 5	-0.56690	0 -	-(33,88327	177160	0,79597	-17.09334	-16.90248	134.24	45.76	58.98	0.75935	0.55533	
C, =(C,)C, =C, C, =(C,)C, =C, C, =(C,)C, =C,	౮	-0.85035	-0.64574	0.15035	0	. 33.96212	0.91771	0.79232	-17.17218	-16.98132	134.09	45.91	58.79	0.76344	0.55124	
C,=C,(W)C, C,=C,(W)C,	U <sup>b</sup>	.0.6063	-0.85035		٥	0.153.92270	0.91771	0.79414	-17,13276	-16.94190	134.16	45.84	58.89	0.76140	0.55328	831
C.(H)C, -C,(H)C,	ئ	-0.85035	-0.15035	0 64574	c	-153.96212	17716.0	0.79232	17,17218	-16.98132	69'28	1176	40.66	1.37597	0,02914	
$C_{r}(H)C_{r}-C_{r}(H)C_{r}$	ئن	-0.64574	-1,13379		•	-153.39522	17719.0	0.81937	-16,60528	-16.41442	90.51	89.49	42.40	נצפנניו	927.00.0	
$C_s(H)C_s = C_sN$	ن	-0,64574	-1.13379	٥	0	-153.19522	17716.0	0.81937	-16.60528	-16,41442	137,29	42.71	61.04	0.70255	0.60208	
$C_s(H)C_s = C_sN$	٠.	.1,13379	-0,60631	0	0	-153,35580	0.91771	0,82132	9159591-	16,37500	137.37	42.63	61.14	0.70038	0 60425	
C,C, - MC,	ئی!	-1.13379	-0.60631	0	0	-153.35580	17710.0	0.82132	-16.56586	-16,37500	138.03	41.97	61.42	0,69080	0.61064	
ב"נ" – אנ" נ"נ" – אנ"	8	-0,60631	-0.60631				0.93084	0.84833	16.03838		139,04	40.96	67.76	0.66083	0.64061	
. N - H (NH)	2	-0.66631	. 1(909'0-	0	0		0.93084	0.84833	-16.03138		119.52	60.48	63,13	0,52338	0.41796	
C,C, - MC,	ن	-0.85035	-0.85035	16309.0-	0	-153,92269	0,91771	0.79414	-17.13276	-16,94189	136.97	43.03	\$0.05	0.72095	0.58048	_

Parameters	Parameters Croup Group	CH (i) Group	C = C Group	Group Group	CH (ii) Group	C-N-C Group	NH Group
5	0.75	-	-	1	1	1	1
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n,	0	0	0	o	0	0	0
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5	0.85252	1	0.85252	_	1	0.85252	0.93613
	-	1	-	-	-	ı	0.75
	0.85252	0.91771	0.85252	0.85252	17716.0	0.84665	17126.0
· v	o	-	0	0	-	0	1
<i>c</i> ,	·	-	4	2	1	4	-
2	0	-	0	0	-	U	
	0.5	0.75	0.5	0.5	0.75	۲0	0.75
ď	0.85252	-	0.85252	-	1	25258.0	1
V, (aV)	-101,12679	-37,10024	-104.37986	-32.93291	-39,09538	-104.73877	-39.48897
V, (cV)	20.69825	13.17125	20.85777	10.10210	13.45505	16806'07	14.45367
T (cV)	34,31559	11.58941	35.96751	9.07768	12.74462	36.26840	15.86820
7, (27)	-17,15779	-5.79470	-17,98376	4.53884	-6.37231	-18.13420	-7.93410
1:(.v. m) (eV)	0	-14,63489	0	-14.63489	-14,63489	O	-14.53414
DE11,200 (20 10) (cV)	0	-1.13379	-2.26759	-1.29147	-2,26758	-2.42526	0
Er (.r. m) (eV)	0	-13.50110	2.26759	-13.34342	-12,36731	2,42526	-14.53414
Er (und) (cV)	-63,27075	-31.63539	-63.27075	-31,63539	-31.63533	-63,27040	-31.63534
$E_r(aloni - aloni, nisp^3, AO)$ (cV)	-2.26759	-0.56690	-2.26759 ·	-1,29147	0	-2.42526	0
Er(sn) (cV)	-65,53833	-32.20226	-65.53833	-32.92684	-31,63537	-65.69600	-31,63537
ω (1018 rad 1.s)	49,7272	26.4826	15.4421	21.8249	28.9084	54,5632	48.7771
E. (cV)	32,73133	17.43132	10.16428	14.36554	19.02803	35.91442	32.10594
R, (aV)	-0.35806	-0.26130	-0.20668	-0.24690	-0.27301	-0.38945	-0.35462
Est (aV)	0.19649	0.35532 Eq. (13.458)	0.17897	2) £2 ( 0   [2]	0.39427	0.11159	0.40696
F. (cV)	-0.25982	-0.08364	-0.11720	-0.18534	-0.07587	-0.33365	-0.15115
E (cV)	0.14803	0.14803	0.14803	0.14803	0.14803	. 0.14803	0.14803
$E_T(imm_d)$ (cV)	-49.54347	-32.28590	-65.77272	-33.11218	-31.71124	-66,36330	-31.78651
E (4. 1) (cV)	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.63489	-14.53414
Eura 19.10 my (cV)	0	-13,59844	0	0	-13,59844	0 .	-13.59844
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Table 15326. The bond angle parameters of indole and experimental values [1]. In the calculation of $\theta$ , the parameters from the mace-dimensional $E$ is $E$ [22].	ingle paramet	ers of indo	ole and ext	verimental va	alues [1]. In the c	aculation of 6	. the parameters (	ion the pre-	alino anala	Past san	-/ 2 1 2		(4)						
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## **ADENINE**

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Adenine having the formula  $C_5H_5N_5$  comprises a pyrimidine moiety with an aniline group and a conjugated five-membered ring which comprises imidazole except that one of the double bonds is part of the aromatic ring. The structure is shown in Figure. 75. The aromatic C=C, C-H, and C=N functional groups of the pyrimidine moiety are equivalent to those of pyrimidine as given in the corresponding section. The  $NH_2$  and  $C_a-N_a$  functional groups of the aniline moiety are equivalent to those of aniline as given in the corresponding section. The CH, NH,  $C_a-N_e$ , and  $N_e=C_e$  groups of the imidazole-type ring are equivalent to the corresponding groups of imidazole as given in the corresponding section. The C-N-C functional group of the imidazole-type ring is equivalent to the corresponding group of indole having the same structure with the C-N-C group bonding to aryl and alkenyl groups.

The symbols of the functional groups of adenine are given in Table 15.327. The geometrical (Eqs. (15.1-15.5) and (15.42)), intercept (Eqs. (15.71-15.78)), and energy (Eqs. (15.6-15.11) and (15.17-15.56)) parameters of adenine are given in Tables 15.328, 15.329, and 15.330, respectively. The total energy of adenine given in Table 15.332 was calculated as the sum over the integer multiple of each  $E_D(c_{map})$  of Table 15.330 corresponding to functional-group composition of the molecule. The bond angle parameters of adenine determined using Eqs. (15.79-15.108) are given in Table 15.332.

Table 15.327. The symbols of functional groups of adenine.

Table 15.32/. The symbols of functional gro	oups of adenine.
Functional Group	Group Symbol
CC (aromatic bond)	3e C=C
CH (aromatic)	<i>CH</i> (i)
$C_{b,c} \stackrel{3e}{=} N_c \qquad C_{a,b} \stackrel{3e}{=} N_b$	$C \stackrel{3\epsilon}{=} N$
$C_a - N_a$	C-N (a)
NH <sub>2</sub> group	. <i>NH</i> <sub>2</sub>
$N_{\epsilon} = C_{\epsilon}$ double bond	N = C
$C_d - N_e$	C-N (b)
$N_dH$ group	NH
СН	CH (ii)
$C_c - N_d - C_e$	C-N-C

	CH (ii) C-N-C Group Group		1,01120 1,30144	1.07021 1.37738	1.076 1.370 (pyrrole) (pyrrole)		0.65928 0.90131
	Group	1,24428	0.94134	0.996270	0.996 (pyrrole)	0.81370	0,75653
	C-N (b) Group	1.82450	1.35074	1,42956		1,22650	0.74033
	N=C Group	1,44926	1,30383	1,37991		0,63276	0.89965
	WH,	1.24428	0.94134	0.99627	0.998 (anilina)	0.81370	0.75653
	C-N(a)	1.81158	1.34595	1.42449	1.431 (anilino)	1.21254	0.74297
nemai values III.	CaN	1.47169	£7072.)	1.34489	1,340 (pyrimidine)	0.74237	0 86345
me and experi	CH (c) Group	1.60061	1.03299	1,09327	1.084 (pyridine)	1,22365	0.64537
bic 13.348. The geometrical bond purameners of agen	ن د د د	1.47348	1,31468	1.39140	1.393 (pyrimidine)	0.66540	0.89223
cole 13.328. The group	Parameter	0 (0,)	در (۵°)	Bond Length	Exp. Bond Length (A)	hc (a,)	,

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Table 15.3	ł
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Table 15.329. The MO to HO intercept geometrical bond parancters of adenine. R is an alkyl group and R.R.R. are H or alkyl groups. E, is E, drow—drom.nup².AO)	cometrical bon	d parameters of	adenine. R is a	m alkyi group an	d R.R.R. Bre	H or alkyl grot	ups E, is E, (	atom - atom, n	.tp'.40).						
Bond	Atam	E <sub>T</sub> (eV) Bond !	(eV) Bond 2	Er (eV) Bond J	E <sub>7</sub> (cV)	Final Total Energy C21p²	18	13	(eV) Final	E(C2sp²) (eV) Final	6 E	9 C	e, 🖭	(a, b,	(a°)
						29									
C,(N,)C,N,H-H	v.	-0.56690	٥	•	0		190660	0.88092	15,37265		7,12	38.26	63.63	0.47034	0.46500
$C_s(N_s)C_s-N_sH_s$	٦,	-0,36690	0.54343	-0.83035	°	133.5GG	והופנ	0.81052	-16.78642	38565.31·	12).90	0. ig	41.95	134737	0.00142
$C_{J}(N_{s})C_{s}-N_{s}H_{s}$	N,	0.55690	0	0	Û		DESCRI	0.XKD92	.13,39265		96.32	83.68	46.43	1,24139	0 03736
C-H (C,H)	5	0.54343	-0.54343	06935.0-	٥	-153,26945	177160	0.X2562	18/47951	-16.29864	78.37	101,73	4514	130081	0.16783
C-H (C,H)	ن	#1 <i>CZC</i> :0-	-0,60631		0	-153.15110	17716.0	031530	2,108,01.	-16.17038	79.01	100.99	41,87	1.19159	0.15860
(H,N) H-N	N	16,000.0-	-0,60631	0	0		0.930H	6.34HZ3	80100791·		119.52	27'09	63.13	0.52238	961170
C,(NH,)C, W,C,	ť	-0.85035	4134333	0095°0-	0	4153,57@6	17710-0	0.81052	-16.78642	988691-	128.54	31.46	58.65	0.76572	0.50501
C,(NH;)C,=N,C, N,C,=N,C,	z' z'	64343	454343	۵	o		0.53084	0,85503	1821021.		130.61	49,39	60.37	0,71418	0.33636
ハンギャン ルンギルン アルボン	٠,٠	64543	4,54343	VE) \$ 6-	c	-153.16045	17714.0	0 K25G2	-(6,4705)	-16,20063	22.021	30.74	9). <del>(</del> 4	0.74PG4	0,52240
C,(N,H)C,=N,C.	ı.	-D.K4D.s	C+C+5'D-	1000 0-	8	-153,61578	171100	0.80%	-16.82584	16.63.49¥	SPEEL	51.55	38.55	0.76752	0.502.81
N, (N, H,)C, -C, (N,)C,	υ' —	-0,48/05	40,54343	06950	o	3636.631-	17716.0	0,81052	-16.78642	+16.59336	134.83	43.15	27.65	0,74304	237163
N,{N,H <sub>3</sub> }C; =C;(N,)C; C;(N,)C;=C;(N,H)N,	6.7	stray e-	\$£05%,p-	G\$77,0-	•	-153,78097	11116.0	0.10076	*14.99103	-16.80017	044	45.36	27.65	0.75398	140950
C, (N,)C, *C, (N,H)N,	5	\$ED\$#(0)	64843-0-	ינו לאוכם ו	5	-153.6157R	0,91771	D x0XC3	-16.823H	16.63.49x	134.77	43.23	29.62	0.74516	0.56952
C,(N,)C,~N,H		-0 PSUDS	61675 0-	16307.0-		-153,6157R	17710.0	Chwar.o	H8ZN 91-	-16,63.49K	137.54	12.46	87,03	0.70488	0.39636
$C_s(H)N_s - C_s(N_s)C_s$ $N_s(H)C_s - N_s(H)C_s$	Ν,	16)oy'ar	16,6,5,6,3	c	5		D.9308LI	0 14(0)	NCBCO.A1-		139,04	40.26	02.76	0.66070	0,64061
N,(H)c,-N,(H)c,		-0.60631	*17.20,0+	O	0	-153,15119	122160	0.83159	-16.36125	-16.17039	131.42	41.54	61.93	04.072.40	0,62203
$C_{j,N_{j}} = C_{j}(H)N_{j,H}$	∵.	-0,9291¥	16309,0-	0	ų	4133,15119	177160	081880	-16 36125	-16.17039	137,93	12.07	22.19	0.68657	22718.0
$C_{s}N_{s}=C_{s}(H)N_{s}H$	ν,	-0-9291X	40,464,59	0	٥		0.930Rd	0,83883	-16.21932		138,20	11.60	62.03	0.67849	n62334
כ'(נ')נ' – א'נ'	N,	40,144.59	#1/26,0-	o	O.		U 9308-L	0,83885	-16.21932		56.19	88,64	43.34	SCIEC.1	0.01939
c. (c.)c n'c.	ن	13 1911	-036035	A NSOTS	c	16037,521.	122160	D.R0076	-16 99 103	-16,80017	17.7x	91,19	40.72	I 3WZNO	003200

		table 19:000. The cherty parameters (c. ) or the chert property of								
Parameters	ري. دور	S day	C = ≥	C-N (a) Group	NH, Group	N = C Group	C - N (b) Group	NH Group	CH (fi) Group	C-N-C Group
<i>y</i>	0.75	-	0.75	_	_		_	-	1	1
'u'	2	-	2	-	2	2	1	-	-	2
n,	0	0	o	0	o	0	0	0	0	0
n,	°	0	0	0	-	0	0	0	0	0
Ċ,	0.5	0.75	0.5	6.5	0.75	5.0	5.0	0.75	0.75	0.5
(,	0.85252	-	0.91140		0.93613	0.85252	1	0,93613	1	0.85252
6,	-	-	-	-	0.75	-	1	0.75	1	ı
6,	0.85252	17710.0	0.91140	0.84665	0.92171	0.84665	0.84665	0.92171	0.91771	0.84665
6,	0	-	0	0	0	0	0	1	1	0
3	2	-	3	2	1	4	7	1	1	4
c,	0	-	0	0	7	0	0	1	1	0
	0.5	0.75	0.5	5.0	51	5.0	0.5	0.75	0.75	0.5
	0.85252	-	0.91140	-	-	0.85252	-	1	1	0.85252
V, (eV)	-101,12679	-37,10024	-102.01431	-32.76465	-78.97795	-103.92756	-32,44864	-39,48897	-39.09538	-104.73877
V, (cV)	20.69825	13.17125	21.41410	10.10870	28.90735	20.87050	10.07285	14.45367	13.45505	20.90891
T (0V)	34,31559	11.58941	34.65890	9.04312	31.73641	35.85539	8.89248	15.86820	12.74462	36.26840
(V) (eV)	67751,71-	-5.79470	-17.32945	4.52156	-15.86820	-17.92770	4.44624	-7.93410	-6.37231	-18.13420
[[ (w m) (eV)	0	-14,63489	0	-14.63489	-14.53414	0	-14.63489	-14.53414	-14,63489	0
DE nin (w. no) (eV)	0	-1.13379	0	-1.13379	0	-1.85836	0.92918	0	-2.26758	-2.42526
E, (v) m) (eV)	0	-13.50110	0	-13,50110	-14,53414	1.85836	-13.70571	-14,53414	-12.36731	2.42526
E(n. no:no) (cV)	٥	0	0	0	-14.53414	0	0	0	0	0
E. (u,10) (cV)	-63.27075	-31.63539	-63.27076	-31.63549	-48.73654	-63.27100	-31.63527	-31.63534	-31.63533	-63.27040
Er (01001 - 01001, 1117) (W)	-2.26759	-0.56690	-1.44915	-1.13379	0	-1.85836	-0.92918	0	0	-2.42526
E, (14) (cV)	-65.53833	-32.20226	-64.71988	-32,76916	-48.73660	-65.12910	-32.56455	-31,63537	-31.63537	-63.69600
(101, rad(s).	49.7272	26.4826	43.6311	0686'11	2186'89	15.4704	21.5213	48.7771	28.9084	54.5632
E. (aV)	32.73133	17,43132	28.71875	7.89138	45.40465	10.18290	14.16571	32,10594	19.02803	35.91442
$\overline{E}_{n}$ (eV)	-0.35806	-0.26130	-0.33540	-0.18211	-0.42172	-0.20558	-0.24248	-0.35462	-0,27301	-0.38945
$\vec{E}_{\rm res}$ (oV)	0.19649	0,35532 Eq. (13,458)	0.19649	0.15498	0.40929 [22]	0.20768	0.12944	0.40696	0.39427 [56]	0.11159
E_ (aV)	-0.25982	-0.08364	-0.23715	-0.10462	-0.21708	-0.10174	-0.17775	-0.15115	-0.07587	-0.33365
E (cV)	0.14803	0.14803	0.09457	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803	0.14803
12 (run) (UV)	-49.54347	-32,28590	-48.82472	-32.87379	-49.17075	-65.33259	-32.74230	-31,78651	-31.71124	-66,36330
E   (aV)	-14.63489	-14.63489	-14,63489	-14.63489	-14,53414	-14.63489	-14.63489	-14.53414	-14.63489	-14.63489
E. wood (4, 10 10) (eV)	0	-13.59844	. 0	0	-13,59844	0	0	-13.59844	-13.59844	0
E. land (cV)	5.63881	3.90454	4.92005	3.60401	7.43973	6.79303	3.47253	3.51208	3.32988	7.82374

Calculated

C.- N.- C Total Bond Energy
(c.Y)

1 70 83735 CH (ii) Table 15.331. The total bond energies of adenine calculated using the functional proup composition and the energies of Table 15.330 compared to the experimental values [2].

Formula Name C = C - N (a)  $NH_1$  N = C C - N (b) NH CH2

Atomia of Ample	3	2	3]	E.	Atom I Hshodiraton	F. Crassman	Aton 2 Hybridizaton	ż	3	٦	ີ ບໍ	'3	5	E <sub>7</sub>	-			Cal. 0	Exp. 0
	(°	9	Alena (o,)		Designation	Almai	Designation	Aren I	Alban 2					(cV)	©		C	 ©	
HNH7	1.\$F26x	i,xezkx		-14.33414	(Table 15.3B)	I	(Tabe: 15.3B) H	0,93613 Eq.	-	-	-	6.75	1,06823		-	+-	+	13.89	113.9 [1] (anilline)
CHINC.	1 вете	2,69190	4,0497	-14.53414	z	-15.95955	v	(Eq.	0,16214 (Eq.	6.73	-	6.75	1,01912	0		<del>                                     </del>		825	511
ZH,C,N, ZH,C,N,	2.06394	234147	3,9497	-14,82573	-	-14,53414	z	0,91771	0.91140 Eq. (15.116)	0.75	-	0.75	0,99312	c				117.63	57
ZH,S,N,	1,02241	2,60766	1990'7	-16.36125	9.	-14.53414	2	0.83159	0.84665 Eq. (13.152)	67.6	_	6.75	1.0111	0			-	ž	126
2H,C,N,		_	L	<u> </u>											F	12235	112.64	125.02	611
ZH,N,C.	1.8826#	2.602#7	4.0497	-14,53414	z	-13.98955	9	0.x4663 (Eq. (13.152))	0,86284 (Eq. (15.64))	0.75	-	27.2	1,10912	0			-	128.35	23
ZNC,N,	2,60766	2.602R7	43359	-16.21952	=	-16.03X38	7	0,13835	0,4433	_	-	-	0,84359	-1.44915	-	-	-	112.64	134.4
ZN,C,N,	2 54147	2,60287	0×2×0	-14.53414	z	-14.53414	z	0.91140 Eq. (15.116)	0.84665 Eq. (13.152)	-	-	-	0.17902	-1.44915			-	13.11	127.8
ZN'C.'N"	2,54147	2,54147	4.5826	-(5,55033		-15,55033	c	0.87495	0,87495		-	-	0.87495	-1,44915		-	F	128.73	128.9
ZN'C."N"	2.54147	2,69190	4.3826	13,912,61	s	-13.39265	7	0.15503	0.18392	-	-	-	0.86947	-1.44915		$\vdash$	-	nu	1.9.1
לא'נ'לנ'	2.70148	2.62936	4381X	-14.53414	z	.15.95955 C <sub>e</sub>	y	0.84665 (Eq. (15.152))	252523	-	_	<i>i</i> -	C(1495R	-1.44915			<u> </u>	\$2011	110.4
ZNF.C.	2,60287	2.62936	4.1952	-14.53414	z	-16.99103 C,	91	0.84665 (Eq. (15.152))	0.10076	-	-	-	0.82371	-1.44915		_		106.60	6.201
7%'C'C'	2.54147	2.62936	17771	-14.53414	z	-16 WIGG	91	0.91140 Eq. (15.116)	0.80076	-	~	-	0.13601	-1.44915				13.73	126.4
75°C'C'	2.54147	2.62936	4.472	-14.53414	z	.16.593103 C.,	91	0.91140 Eq. (15.116)	0.10076	-	-	-	0.85608	-1.44915		-	_	£7.611	182
כאיני,כי	2.69190	2.62936	4.5607	-14.53414	· Z	-16,52644 C,	71	0.91140 Eq. (13.116)	0,13377	-	-	-	0.86734	-1,44915		$\vdash$	-	16,711	1.22
ZN,C,C,	2,70148	2.62936	4.8990	-14.53414	z	.14.82575 C,	1	0.91140 E4. (15.116)	17716.0		-	-	0.91456	-1,44915		-		55.001	132.8
ZC,N,C.	2,7014K	2,60766	4.2661	-17.92022	12	17.92022	82	0.75924	0,75924	-	-	-	0.75924	-1.35836		$\vdash$	-	106,93	103.3
ZC.'N'C.	2.60287	2,603.87	12661	-17.75502	25	-17.73502	52	0.76631	0.76631	_	_	-	0.76631	-1.85836		_		10.01	1001
מב'א'נ."	2.54147	2.54147	4.3589	-17.40K69	12.	-17.75502	52	0.78155	0,76631	-	-	-	ó.77393	-1,85836		-		118.09	1113
"," N, C."	2,54147	2,54147	4,3704	-17,71560	74	-17,40869	12	0.76801	0.78155	-	-	-	0,77478	-1.85836				118.59	118.6
	2,62936	2,62936	4.4721	.17.71560	24	-17,54871	65	0.76401	0.193.00	-	-	_	0.78071	.1 858.56			-	114.53	1

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While the claimed invention has been described in detail and with reference to specific embodiments thereof, it will be apparent to one of ordinary skill in the art that various changes and modifications can be made to the claimed invention without departing from the spirit and scope thereof.

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